DIPLAZIUM ESCULENTUM LEAF AS A NATURAL COAGULANT AID IN LANDFILL LEACHATE TREATMENT

by

NOOR AINEE BINTI ZAINOL

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LIST OF ABBREVIATIONS

Alum	Aluminum sulphate
APHA	American Public Health Association
AWWA	American Water Works Association
BF	Breakage Factor
BOD	Biochemical Oxygen Demand
CA	Coagulation Activity
COD	Chemical Oxygen Demand
FTIR	Fourier Transform Infrared
DEaqs	Extract of *Diplazium esculentum* leaves with water
DEpowd	Extract of *Diplazium esculentum* leaves in powder formed with acid treated
FTIR	Fourier Transform Infrared
H_2SO_4	Sulphuric Acid
IEP	Isoelectric point
KLS	Kulim Landfill Site
KSLS	Kuala Sepetang Landfill Site
MSW	Municipal Solid Waste

NaOH	Sodium Hydroxide
NH_3-N	Ammonia-N
NTU	Nephelometric Turbidity Unit
PACI	Polyaluminum chloride
PZC	Point of Zero Charge
RE	Removal Efficiency
RF	Recovery Factor
rpm	rotation per minute
SF	Strength Factor
SP	Sediment Percentage
SS	Suspended Solid

DAUN *DIPLAZIUM ESCULENTUM* SEBAGAI BAHAN BANTU PENGUMPAL SEMULAJADI DALAM OLAHAN LARUT LESAPAN

ABSTRAK

Olahan secara penggumpalan-pengelompokan telah dikenalpasti sebagai salah satu kaedah alternatif yang diaplikasikan dalam perawatan larut lesapan. Namun demikian, bahan pengumpal yang digunakan dalam proses ini kebanyakan terdiri daripada bahan pengumpal kimia dan berupaya memberikan impak buruk kepada kualiti alam sekeliling. Oleh itu, penghasilan bahan pengumpal yang mesra alam adalah perlu agar pembangunan mapan dapat tercapai. Penggunaan daun pucuk paku sebagai bahan pengumpal masih belum dibincangkan dalam literatur. Dalam kajian ini, kebolehupayaan ekstrak daun pucuk paku iaitu *D. esculentum* aqueous (DEaqs) dan *D. esculentum* powder (DEpowd) untuk bertindak sebagai bahan pengumpal dan bantu pengumpal dengan polyaluminum chloride (PACI) dinilai dengan menggunakan larut lesapan stabil dari Tapak Pelupusan Kuala Sepetang (KSLS) dan Tapak Pelupusan Kulim Kedah (KLS) melalui Ujian Balang. Di samping itu, kajian ini juga menguji sifat-sifat kimia ekstraknya seperti titik isoelektrik, berat molekul, spektra dari Fourier Transform Infrared dan analisis unsur. Dikenali sebagai polimer bermolekul tinggi, Deaqs (221 kDa) dan Depowd (275 kDa) bertindak sebagai pengumpal anionik dan mampu untuk menggalakkan proses pengumpalan larut lesapan yang tepu dengan zarah negatif. Kumpulan berfungsi yang mendorong proses penggumpalan-pengelompokan oleh DEaqs dan DEpowd adalah karboksil, hidroksil dan amina, di mana kesemua kumpulan berfungsi ini mengandungi ikatan hidrogen dalam molekul. Analisis Ujian Balang menjurus kepada aktiviti penggumpalan dan kecekapan penyingkiran pepejal terampai (SS), kekeruhan,

warna, keperluan oksigen kimia (COD), dan ammonia-N. Selain itu, keadaan operasi semasa proses penggumpalan-pengelompokan, kekuatan flok dan peratus enapcemar turut dikaji. Keputusan menunjukkan bahawa 200 mg/L DEaqs pada pH 12 dalam sampel KLS menunjukkan kecekapan penyingkiran yang lebih tinggi dengan penyingkiran masing-masing, 94%, 92% dan 43% untuk SS, kekeruhan dan ammonia-N berbanding PACI. Disamping itu, pada kepekatan 1000 mg/L dan pH 10, Deaqs menghasilkan penyingkiran yang tertinggi untuk ammonia-N (69%) berbanding PACI (38%) dalam sampel KSLS. Sejumlah 50% isipadu PACI dapat dikurangkan dari dos optimum asal PACI apabila dos gabungan Deaqs dan Depowd yang digunakan adalah kurang dari 1000 mg/L telah menunjukkan kesan ketara terhadap kadar penyingkiran bagi semua parameter diukur dalam sampel KSLS. Sementara itu, flok yang dibentuk oleh 1000 mg/L PACI dan 500 mg/L DEaqs menunjukkan keupayaan yang lebih baik untuk menahan daya ricihan dengan faktor kekuatan yang lebih tinggi, 121 berbanding PACI sahaja, 86. Oleh itu, ekstrak dari daun pucuk paku sebagai bahan pengumpal dan bantu pengumpal boleh dicadangkan sebagai alternatif dalam olahan larut lesapan melalui kaedah penggumpalan-pengelompokan.

DIPLAZIUM ESCULENTUM LEAF AS A NATURAL COAGULANT AID IN LANDFILL LEACHATE TREATMENT

ABSTRACT

Coagulation–flocculation treatment is recognized as one of the alternative methods for treating landfill leachate. However, the conventional coagulants utilized in this process may adversely impact the environment because most are chemical-based and not environmentally friendly. Hence, the production of an environmentally friendly coagulant is necessary to achieve sustainable development. The use of extracts from *Diplazium esculentum* leaves as coagulant and coagulant aid has not been discussed in literature. In this research, the capability of extracts from *D. esculentum* leaves, namely, *D. esculentum* aqueous (DEaqs) and *D. esculentum* powder (DEpowd), to act as coagulant and coagulant aid in combination with polyaluminum chloride (PACl) was evaluated using stabilized leachate from the Kuala Sepetang Landfill Site (KSLS) and the Kulim Landfill Site (KLS) through a jar test. This research also examined its chemical characteristics (i.e., isoelectric point, molecular weight, Fourier Transform Infrared, and elemental analysis). Identified as polymers with high molecular weight, DEaqs (221 kDa) and DEpowd (275 kDa) act as anionic coagulants and are capable of promoting the coagulation process in leachate saturated with negative particles. The main functional groups that induce the coagulation–flocculation process by DEaqs and DEpowd are carboxyl, hydroxyl, and amine groups, which all contain hydrogen in their molecules. Jar test results were analyzed based on the coagulation activity and removal efficiency (RE) of suspended solids (SS), turbidity, colour, chemical oxygen demand (COD), and ammonia-N. Operating conditions during coagulation–flocculation, floc strength, and sediment percentage characteristics were also studied. Results indicated that 200 mg/L DEaqs

at pH 12 in KLS leachates showed the highest removal with 94%, 92%, and 43% of SS, turbidity, and ammonia-N, respectively compares to PACI . In addition, at 1000 mg/L and pH 10, DEaqs yielded the highest removal for ammonia-N (69%) compared to PACl (38%) in KSLS leachates. A 50% reduction in the volume of PACl from its optimum dosage, with the DEaqs and DEpowd dosages below 1000 mg/L, exhibited a synergic effect of all the measured parameters in KSLS leachates. Flocs formed by 1000 mg/L PACl in conjunction with 500 mg/L DEaqs also displayed better shear resistance with a higher strength factor of 121, which was significantly higher than the factor of 86 for PACl alone. Therefore, the use of extracts from *D. esculentum* leaves as coagulant and coagulant aid can be proposed as an alternative in the treatment of landfill leachate via coagulation–flocculation.

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Over the past decades, Malaysia has thrived with rapid economic growth and development. Such growth has changed consumption patterns and lifestyles and improved the public standard of living. These changes have led to a massive amount of waste generation, giving rise to environmental concerns regarding their final disposal in landfills.

In Malaysia, approximately 80% to 90% of generated municipal solid wastes (MSW) are transferred to landfills for disposal (Johari et al., 2012). Landfilling has been demonstrated the most economic MSW disposal method compared to other means of disposal methods such as incineration and composting etc. (Renou et al., 2008). Despite its advantages, the method has one major concern: the generation of leachate produced from landfills.

Presently, 296 landfill sites are distributed all over Malaysia. Of this number, 123 sites are already closed and the remaining 173 are still operating, including 9 sites that are classified as sanitary landfills (National Solid Waste Management Department, 2013). Most of the landfill sites are unsanitary. As leachate flows away from a landfill, it causes serious pollution to surface water and groundwater sources which is harmful to the natural ecosystems and human health.

Landfill leachate is produced from a combination of water percolation and biodegradation activities (decomposition of biodegradable materials) in a landfill. It

is a highly polluted wastewater. Many factors affect the quality and quantity of leachate produced, including waste composition, landfill age, site hydrogeology, specific climate conditions, moisture routing through the landfill, and landfill design and operation (Ghafari et al., 2010; Aziz et al., 2004). Leachate pollution in Malaysia is very serious. This is due to the high generation of landfill leachate in tropical areas is mainly dependent on the high amount of rainfall (Robinson, 2005; Lema et al., 1988).

The presence of high concentrations of these parameters in landfill leachate over a long period of time is one of the most important problems faced by landfill operators. In addition, the high level of NH_3-N is the main factor that enhances algal growth and promotes eutrophication because of the decrease in dissolved oxygen (Kamaruddin et al., 2013; Kurniawan et al., 2006). Consequently, NH_3-N is a major toxicant to living organisms (Kamaruddin et al., 2013; Bashir et al., 2010; Kurniawan et al., 2006).

Researchers worldwide are still searching for a total solution to the leachate problem. Thus, a better understanding of the characteristics of the leachate produced is very important in determining specific leachate treatment. Stabilized leachate, indicated by a low biochemical oxygen demand (BOD_5/COD) ratio (i.e., low biodegradability) and seen in many landfills in Malaysia, is particularly difficult to treat biologically (Bashir et al., 2010; Mohajeri et al., 2010). Therefore, chemical and physical method needs to be applied.

Coagulation-flocculation is one of the treatment options used in treating stabilized leachate. Generally, it has been employed as pre-treatment prior to biological or reverse osmosis step or as a final polishing treatment step in order to

remove non-biodegradable organic compounds and heavy metals from landfill leachate (Syafalni et al., 2012; Ghafari et al., 2010; Foo and Hameed, 2009; Renou et al., 2008; Aziz et al., 2007a; Aziz et al., 2004; Rivas et al., 2004; Tatsi et al., 2003; Amokrane et al., 1997).

Quite a number of previous literature such as Apostol et al. (2011); Liang et al. (2009); Bucişcanu et al.(2008); Duan and Gregory, (2003) focused on coagulation-flocculation process using chemical based (inorganic) coagulants like alum and ferric salts. Reported studies mainly focused on the application of alum or ferric salts to treat leachate and synthetic wastewater consists of humic acid, kaolin, dyes, phosphate and magnesium in combination or alone contributing to BOD5, COD, colour, turbidity and SS.

There are doubts about the advisability of introducing chemical coagulants to the environment (Zouboulis et al., 2004; Mallevialle et al., 1984). For instance, Bi et al. (2004) and Sanghi et al. (2002) also indicated several serious drawbacks of using aluminum based coagulants (the major component of PACI and alum), such as Alzheimer's disease, Parkinson's disease, and similar health-related problems associated with residual aluminum concentrations in treated water.

Nowadays, increased attention has been paid to the application of natural coagulants to alleviate the problems of water and wastewater treatment in developing countries. However, there is not a great deal of published information on the application of natural coagulants for wastewater purification. Many findings from existing literature (Anastasakis et al., 2009; Beltràn-Heredia and Sànchez-Martin, 2009b; Sciban et al., 2009; Zhang et al., 2006; Okuda et al., 2001a and 2001b; Aziz et al., 2000) mostly tends to study the removals of SS and turbidity in synthetic

water, streams or river water sources, municipal effluent and dyes wastewater. However, to date, no natural coagulant has been carried out for the treatment of landfill leachate.

Natural coagulants of vegetable and mineral origin were in use in water and wastewater treatment before the advent of chemical based coagulants like aluminum and ferric salts. Previous studies, however, have not determined whether such natural coagulants are economically and environmentally more acceptable than chemical based coagulants. Natural coagulants are biodegradable and cost effective for developing countries since they can be locally grown and have a wider effective dosage range for flocculation of various colloidal suspensions in water purification (Sanghi et al., 2006).

1.2 Problem Statement

Characteristics of landfill leachate are very complex. The leachate normally contains high amounts of pollutants, such as dissolved organic matter, nitrogen, phosphate, benzene, phenol, and heavy metals (Abbas et al., 2009; Kjeldsen et al., 2002; Bagchi, 1990). The levels of COD, colour and ammonia-N (NH_3-N) are also high. For example, the average values of NH_3-N in Pulau Burung , Kulim and Kuala Sepetang landfill sites are 1380, 503 and 996 mg/L, respectively (Umar et al., 2010). The allowable discharge limit is 5 mg/L according to the Environmental Quality Regulations 2009, Malaysia Environmental Act 1974 (Act 127: Control of Pollution from Solid Waste Transfer Station and Landfill).

Coagulation-flocculation is one of the treatment options used in treating landfill leachate. However, the coagulation-flocculation process normally involves

the use of chemical based (inorganic) coagulants like alum and ferric salts. Commercially available synthetic polymers such as polyacrylamides are also used as coagulant aid to improve the settling characteristics and toughness of flocculated particles and hence enhancing the treatment efficiencies. As landfill leachate is a highly polluted wastewater, the amount of coagulant needed is normally quite significant. Inorganic coagulant dosage between 5,000 mg/L to 10,000 mg/L is quite common. This leaves high Fe and Al residuals in the final effluent and the sludge problems. Further treatment is necessary and this adds to the overall cost of treatment.

Due to the drawbacks in the applications of these chemical based coagulants, a few focuses have been made on the application of natural coagulants and coagulant aids as alternative to the current practice. Several studies used synthetic polyelectrolytes as coagulant aid (Lee and Westerhoff, 2006; Aguilar et al., 2005; Zouboulis et al., 2004; Kam and Gregory, 2001). To date, limited study has been carried out to use natural coagulant and coagulant aid for the treatment of landfill leachate.

Diplazium esculentum or pucuk paku belongs to the botanical group Pteridophyta. It is widely available near river and swamps areas in Malaysia, India, China, Cambodia, Laos, Thailand, and Vietnam. It usage as coagulant and coagulant aid has never been reported in literature to date. Its extraction procedures and characterizations are not well described. Since Malaysia is well endowed with many kinds of natural polymers that are widespread in nature, therefore, exploring an alternative natural coagulant is preferable to counteract the aforementioned drawbacks. In addition, by using locally available material, the treatment cost could

be reduced. Many developing countries could hardly afford the high cost of imported chemicals due to low availability of chemical coagulants.

This research aims to investigate the efficiency of *Diplazium esculentum* as a coagulant aid to the Polyaluminum chloride (PACI) as main coagulant, for the treatment of landfill leachate from two non-sanitary landfill sites in Malaysia; namely Kulim Landfill Site (KLS) and Kuala Sepetang Landfill Site (KSLS). Both landfills are categorized as an anaerobic landfill where the wastes are compacted by layers. The landfills are not equipped with gas ventilation systems and the leachates produced are flown into leachate pond with no other treatments. The leachate are stabilized (BOD/COD < 0.1) and highly concentrated and difficult to be treated biologically. The levels of SS, colour, COD and NH_3-N in the leachate is high. To date, limited studies have been undertaken for the treatment landfill leachate both sites. PACI has never been investigated as coagulant to treat leachate from KLS and KSLS.

1.3 Research Objectives

The research aimed for the first time to evaluate the efficiencies of *D. esculentum* (pucuk paku) leaf extract as coagulant and coagulants aid in stabilized landfill leachate treatment by using coagulation-flocculation process. The specific objectives of this study include the following:

i. To characterize the extracts of *D. esculentum* leaf with water (DEaqs) and acid treated (DEpowd) based on isoelectric point (IEP), molecular weight and functional group properties.

ii. To determine optimum operating conditions based on rapid mixing time (T_R) and intensity (ω_R), slow mixing time (T_s) and intensity (ω_S), and settling time (T_{SET}) of PACI, DEaqs and DEpowd as primary coagulant to remove turbidity, SS, colour, COD, and NH_3-N.

iii. To determine the optimum pH and dosage of DEaqs and DEpowd as coagulant and as coagulant aid in the presence of PACl to remove turbidity, SS, colour and NH_3-N.termine

iv. To determine possibility of reducing the primary coagulant by adding the DEaqs and DEpowd as coagulant aid.

v. To evaluate the effects of DEaqs on floc formation and sediment percentage (SP) when used as coagulant aid.

1.4 Scope of Research

This study mainly focused on laboratory work as indicated below:

i. Raw landfill leachates from KLS and KSLS were first characterized by collecting leachate samples during a 26-month period from October 2010 to November 2012, including both dry and wet days.

ii. The performance of *D. esculentum* as coagulant aid was determined by means of a standard jar test in a laboratory.

iii. Only *D. esculentum* leaves (pucuk paku) that belong to the Family *Athyriaceae* were tested for coagulation efficiency.

iv. The only working parameters used were turbidity, SS, colour, COD, and NH_3-N removal by PACl, DEaqs, and DEpowd.

v. The possible reduction using PACl as the main coagulant was only conducted at two different dosages: (a) 2000 and 1000 mg/L for KSLS, and (b) 500 and 200 mg/L for KLS.

vi. The examination of sludge property (formation, breakage, and regrowth of flocs) was only performed for KSLS samples on the following experimental conditions: (a) 2000 mg/L PACl, (b) 2000 mg/L PACl + 1000 mg/L DEaqs, and (c) 1000 mg/L PACl + 500 mg/L DEaqs. The use of these conditions was the result of an insufficient sludge volume produced in KLS samples after the coagulation–flocculation process.

1.5 Organization of Thesis

This thesis consists of the following five chapters:

Chapter 1 Introduction: An introduction and definition about the municipal solid waste, landfill leachate and coagulation-flocculation process is presented. Problem statements that provide the basis and rational to identify the research directions is given in this chapter. The main aim and specific objectives of the present study are elaborated together with the scope of the study to be covered.

Chapter 2 Literature review: In this chapter, it reviews the waste disposal problem in Malaysia, generation and characteristics of the leachate and the development in leachate treatment methods especially coagulation-flocculation. Chemical based and plant based coagulants and the mechanisms of coagulation are also presented.

Chapter 3 Materials and methods: This chapter presents the site location and characteristics, sampling, experimental procedures, materials, instruments and analytical methods of parameters.

Chapter 4 Results and discussion: The first section in this chapter describes the characteristics of leachate. The second section discusses the characterization of *Diplazium esculentum* and followed by the discussion on operating conditions in coagulation-flocculation process. The fourth section reports the effects of the pH and dosage for the studied coagulants i.e. PACI, DEaqs and DEpowd are compared. The fifth section reports the effect of removal efficiency of DEaqs and DEpowd as coagulant aids. Finally, the flocs formed and sediment percentage are characterized as supporting evidences of successful coagulation.

Chapter 5 Conclusions and recommendations: In this chapter, the conclusions of the findings in the current study are presented. Furthermore, the recommendations based on the study findings are presented for future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter gives general overview on the municipal solid waste (MSW) problems in Malaysia, waste disposal by landfilling, leachate generation and its treatment options and finally focuses on coagulation-flocculation in leachate treatments.

2.2 Municipal Solid Waste (MSW)

Municipal solid waste (MSW) has become a major concern in our society nowadays. Waste is defined as "lack of use" or value, or "useless remains" (McDougall et al., 2001). Dixon and Jones (2005) defined MSW as a mixture of wastes that primarily originates from residential and commercial establishments. While The Malaysian Solid Waste and Public Management Act of 2007 (Act 672) defined MSW as any substance that require disposal because it is broken, worn out, contaminated or physically spoiled.

Since 1994, the population of Malaysia has grown at an annual rate of 2.4% or 600,000 (Manaf et al., 2009). The average amount of MSW generated in Malaysia was 0.5-0.8 kg/person/day, which increased to 1.7 kg/person/day in major cities (Kathirvale et al., 2003). Consequently, with the existing trend, this amount is expected to reach more than 31,000 tons by year 2020 (Manaf et al., 2009). The most

important factors that contribute to an increased rate of MSW generation and disposal are the increasing population growth and the rapid economic development of a country.

As the amount of MSW increases, studying the compositions of MSW becomes more important and compulsory. The composition of waste in Malaysia mainly constitutes organic matter. Table 2.1 illustrates the typical composition of MSW in Malaysia from different researchers and sites. As seen in the table, more than 40% of the waste is organic, followed by paper and plastic. Most organic wastes are generated from processed kitchen wastes and food wastes. According to Kathirvale et al. (2003), 80% of the overall weight of waste produced in Malaysia consists of food, paper and plastic.

Several external factors, including tropical climate and heavy rainfall throughout the year, make the characteristics of Malaysian MSW different from other countries. In addition, Malaysians generally dispose their garbage in uncovered containers that allow rainfall to accumulate and result in leachate, high moisture content and low calorific value of the waste (2200 kcal/kg) (Kathirvale et al., 2003). In literature, moisture content value that range from 15.35 %, 52.6 % and 66.2 % to 78 % were documented (Nas and Byram, 2008; Mathews, 2003; Hassan et al., 2001).A high concentration of organic waste contains high moisture, and the bulk density more than 200 kg/m^3 (Manaf et al., 2009). Therefore, weather, type of waste and moisture content affect bulk density and other MSW characteristics.

Table 2.1: Composition of MSW at various sites in Malaysia

References	Site (Year)	Organic (%)	Mix Paper (%)	Plastic (%)	Glass (%)	Metals (%)	Textiles (%)	Wood (%)	Others (%)
Saeed et al., 2009	Kuala Lumpur (1975)	63.70	11.70	7.00	2.50	6.40	1.30	6.50	0.90
	Kuala Lumpur (1980)	78.05	11.48	0.57	0.57	3.16	3.16	2.58	0.43
	Kuala Lumpur (1990)	40.80	30.00	9.80	3.00	4.60	2.50	3.20	6.10
	Kuala Lumpur (1995)	61.76	12.16	5.27	5.27	6.89	2.84	0.00	5.81
	Kuala Lumpur (1996)	45.70	29.90	9.00	3.90	5.10	2.10	-	4.30
	Shah Alam (1996)	47.80	20.60	14.00	4.30	6.90	2.40	-	4.00
	Kuala Lumpur (2000)	68.67	6.43	11.45	1.41	2.71	1.50	0.70	7.13
Hassan et al., 2001	Kuala Lumpur (2001)	68.40	6.30	11.80	1.40	-	1.50	0.70	9.90
Kathirvale et al., 2003	Kuala Lumpur (2003)	37.40	16.40	18.90	2.60	-	3.40	3.70	17.60
JICA, 2006	Malaysia (2004)	49.30	17.10	9.70	3.70	-	-	-	20.2
Chua et al., 2011	Bukit Tagar Landfill (2005)	47.5	18.5	-	-	-	2.13	4.41	27.46

Table 2.1: Continued

References	Site (Year)	Organic (%)	Mix Paper (%)	Plastic (%)	Glass (%)	Metals (%)	Textiles (%)	Wood (%)	Others (%)
Bashir, 2007	Pulau Burung Landfill Site, Penang	35.72	16.61	22.19	3.20	2.44	5.10	0.58	14.16
Ngoc and Schnitzer, 2009	Malaysia	62.00	7.00	12.00	3.00	6.00	-	-	10.00
Aziz , et al., 2010	Kulim Landfill Site, Kedah (2010)	45.00	7.00	24.00	3.00	6.00	-	-	15.00
Yatim and Arshad, 2010	Petaling Jaya (2010)	43.5	22.70	25.20	2.60	-	0.90	-	5.10

2.3 Classification of landfill in Malaysia

Presently in Malaysia, landfill is the main option used for the disposal of MSW and most of the landfill sites are open dumping (Manaf et al., 2009). Hence, the management and improvement of landfill sites are imperative. Landfill sites are classified based on two categories: operational purpose and decomposition processes that occur in a landfill (Idris et al., 2004). The details of these classification systems are featured in the following sections.

2.3.1 Classification Based on Operational Purpose

The various levels of improvement for this classification system can be achieved in four stages:

a. Level 1 - controlled tipping

   Solid wastes are covered daily with soil, sand, or small rocks to prevent fire and the emission of unpleasant smells.

b. Level 2 - sanitary landfill with daily cover

   This type of landfill is the same as the one in Stage 1, but with additional criteria such as a perimeter fence and a surface drainage system to drain fluids out of the landfill area.

c. Level 3 - sanitary landfill with a leachate recirculation system

   The landfill is equipped with a waterproof layer that prevents the leachate from being absorbed by the soil, which could also further pollute the underground water. A network of pipelines is designed vertically and horizontally. These pipelines are used to flush out the gas and leachate produced in the decomposition of solid waste. The leachate collection pond is also designed for this type of landfill. The collected leachate is aerated and recycled back to the landfill to enhance the chemical decomposition process.

d. Level 4 - sanitary landfill with a leachate treatment system

   This type of landfill is the well-designed landfill because it is equipped with a leachate treatment system.

2.3.2 Classification Based on Decomposition Process

In this classification system, microbial degradation environment is determined while its aeration and leachate collection measures are evaluated for further distinction. This classification system is divided into five types as follows.

a. Anaerobic landfill- Solid wastes are filled in an excavated area of a plain field. Wastes are filled with water in anaerobic condition.

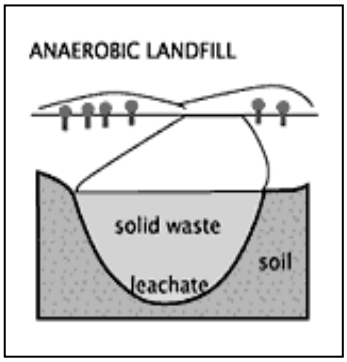

Figure 2.1: Anaerobic landfill (Source: Shimaoka et al., 2000)

b. Anaerobic sanitary landfill- Waste is covered daily, and the landfill shape is like a sandwich. The condition of solid waste is the same as with the anaerobic landfill.

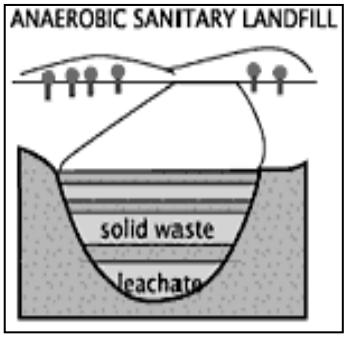

Figure 2.2: Anaerobic sanitary landfill (Source: Shimaoka et al., 2000)

c. Improved anaerobic sanitary landfill - This kind of landfill has a leachate collection system at the bottom of the landfill site similar to that in the anaerobic sanitary landfill. The conditions are still anaerobic, but moisture content is significantly less than in the anaerobic sanitary landfill.

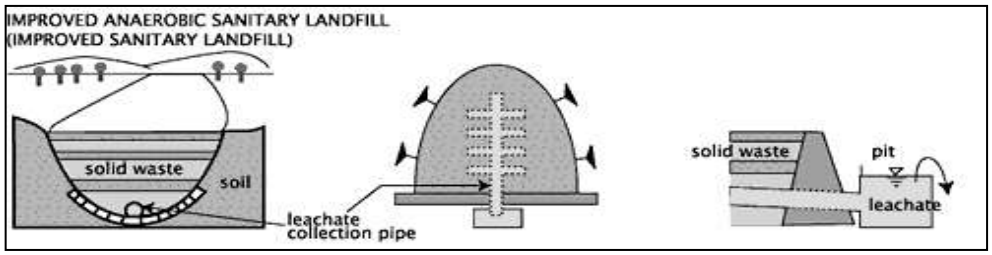

Figure 2.3: Improved anaerobic sanitary landfill (Source: Shimaoka et al., 2000)

d. Semi-aerobic landfill - The leachate collection duct is bigger than the one in the improved sanitary landfill. The duct opening is surrounded by air, and the duct is covered with small crushed stones. Moisture content in solid waste is small. Oxygen is supplied to the solid waste from the leachate collection duct.

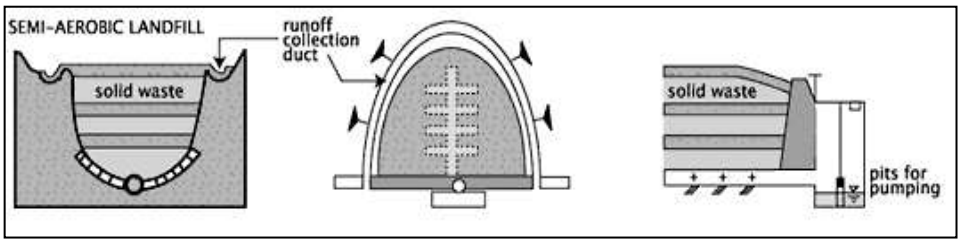

Figure 2.4: Semi-aerobic landfill (Source: Shimaoka et al., 2000)

e. Aerobic landfill - In addition to leachate collection pipes, air supply pipes are attached and air is forced to enter the solid waste. In this condition, the landfill becomes more aerobic than the semi-aerobic landfill.

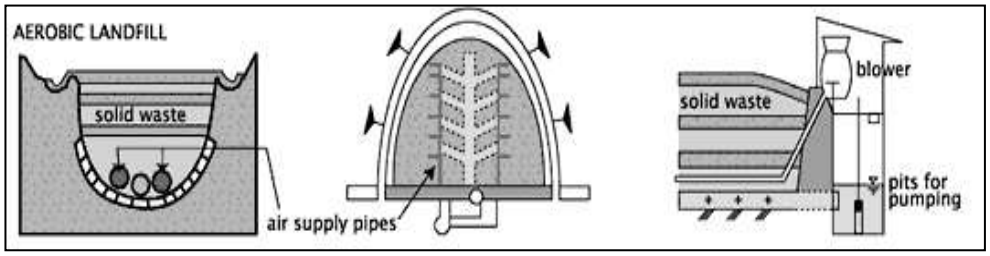

Figure 2.5: Aerobic landfill (Source: Shimaoka et al., 2000)

2.4 Landfill Leachate

When waste is deposited in a landfill cell, water content from inside the waste, rainwater, and surface water drainage will lead to leachate production. The amount of leachate produced depends on the amount of water that percolates through the landfill cell and mixes with the waste.

More water content in the waste leads to the production of more leachate, which will seep through the landfill either vertically or laterally. Lateral movement will happen when an immediate impermeable cover is used daily, and this movement may cause surface water contamination. Vertical movement will bring the leachate pass through rocks and to the aquifer. The leachate, which picks up soluble heavy materials such as heavy metals and acids in the waste, will eventually contaminate the groundwater. If this groundwater is extracted as drinking water supply, it can be hazardous to humans.

2.4.1 Leachate Generation

Generally, decomposition in landfill can be divided into three categories: physical, chemical and biological decomposition. Their progress rates are highly dependent on the waste characteristics. Physical decomposition occurs during segregation and mechanical size reduction while chemical decomposition involves processes like combustion, pyrolysis and gasification. Biological decomposition includes aerobic and anaerobic degradation. This process is initiated right after the waste is transferred into the landfill. In fact, the waste has started undergoing biodeterioration right after the waste is being thrown away.

Decomposition in landfills is divided into five phases. The generalized phases in landfill leachate and gas generation are as follows: Phase I - initial adjustment phase called enzyme hydrolysis phase, Phase II - transition or fermentation phase, Phase III - acidogenic or acetogenic phase, Phase IV - methane fermentation, and Phase V - maturation phase (Tchobanoglous et al., 1993). Throughout the process, the heterogeneous nature of waste may cause all the different stages to progress simultaneously until all the wastes reach Phase V and stabilization in the landfill is achieved. Figure 2.6 briefly illustrates the phase sequence effects on gas composition and leachate characteristics.

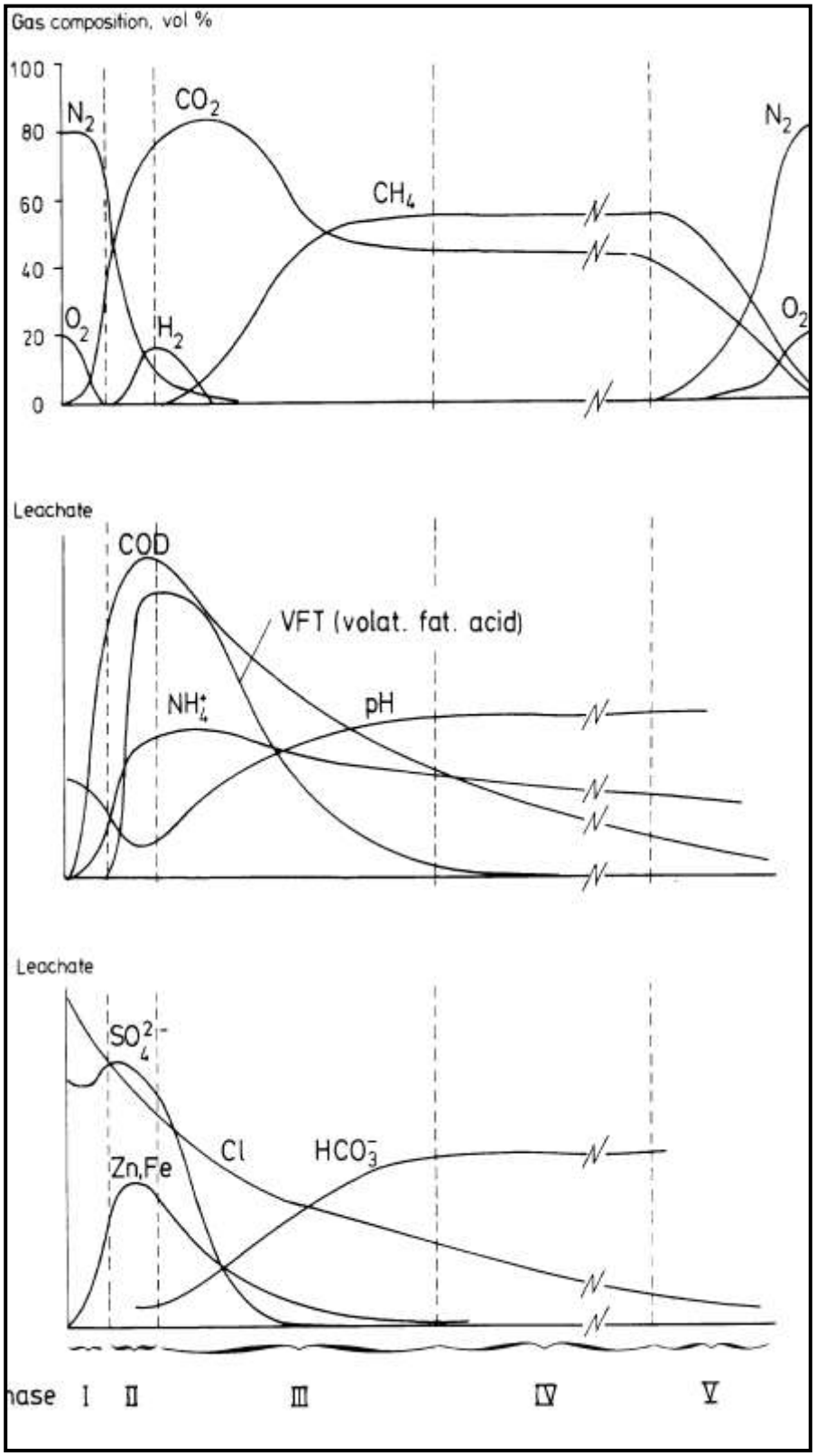

Figure 2.6: Illustration of developments in leachate and gas in a landfill cell

(Source: Christensen and Kjeldsen, 1989)

In the initial adjustment phase, the organic biodegradable materials undergo microbial decomposition in aerobic conditions because of a specific amount of air trapped within the landfill. In this phase, the amount of generated leachate is not substantial.

Phase II is the transition phase where the anaerobic degradation processes of acid fermentation and acetogenesis start to take place. These two processes result in the production of acid in the landfill, which lowers the pH value of the leachate and raises the concentration of volatile fatty acids referred to as total volatile acids. A concurrent increase of inorganic ions (e.g., Cl^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+) also happens because easily soluble material leaches in an acidic condition.

During Phase III, methanogenic bacteria grow and microbial activities accelerate with the production of a significant amount of organic acids and a lesser amount of hydrogen gas. Bacterial growth is initially suppressed by the acidic environment. At this stage, the pH of the leachate will often drop to 5 or lower because of the presence of organic acids and carbon dioxide (CO_2) (Tchobanoglous et al., 1993). The dissolution of organic acids will significantly increase the BOD_5, COD, and conductivity of the leachate. The BOD value is usually more than 10,000 mg/L, and the ratio of BOD_5 to COD is 0.7 (McBean et al., 1995). Ammonia level in this phase increases (500 mg/L–1000 mg/L) while oxygen decreases and a small amount of heat is released (McBean et al., 1995). Low pH value also results in the solubility of a number of heavy metal constituents.

In Phase IV, methanogenic microorganisms have established themselves in the system. The pH value within the landfill will increase to neutral levels ranging from 6.8 to 8 because of the conversion of acids and hydrogen gas to CH_4 and CO_2 in

this phase (Tchobanoglous et al., 1993). In turn, when leachate forms, its pH will increase, and the BOD_5 and COD concentrations as well as the conductivity value of leachate will be reduced. With higher pH values, fewer inorganic constituents are solubilized; thus, the concentration of heavy metals present in the leachate will also be reduced (Tchobanoglous and Kreith, 2002).

The final phase occurs after the readily available biodegradable organic materials have been converted to CH_4 and CO_2 in the previous phase. As moisture continues to migrate through the waste, portions of the biodegradable material that were previously unavailable will be converted. The rate of landfill gas generation diminishes significantly in Phase V because most of the available nutrients have been removed with the leachate during the previous phases, and the substrates that remain in the landfill are gradually becoming biodegradable. During this phase, the leachate will often contain humic and fulvic acids, which are difficult to process biologically (Tchobanoglous and Kreith, 2002). Table 2.2 shows the ranges of several leachate parameters according to the different phases of the biological process.

Table 2.2: Ranges of leachate compositions as a function of the landfill stabilization

Parameter	Transition	Acid Formation	Methane Fermentation	Maturation
COD (mg/L)	480-18,000	1500-71,000	580-9760	31-900
Total volatile acids (mg/L as acetic acid)	100-3000	3000-18,800	250-4000	0
NH_3-N (mg/L)	120-125	2-1030	6-430	6-430
pH	6.7	4.7-7.7	6.3-8.8	7.1-8.8
EC (µS/cm)	2450-3310	1600-17,100	2900-7700	1400-4500

(Source: Worrell and Vesilind, 2010)

2.4.2 Leachate compositions and characteristics

Landfill leachate mainly consists of large amounts of organic matter, including dissolved organic matter, phenol, ammoniacal-nitrogen, phosphate, heavy metals, sulfide, hardness, acidity, alkalinity, salinity, solids, inorganic salts, and other toxicants (Foul et al., 2009; Aziz et al., 2009; Renou et al., 2008; Kang et al., 2002; Wang et al., 2002). The complexity of these characteristics makes leachate difficult to manage. Landfill leachate can be classified based on the decomposition process of the waste and the characteristics of the leachate. Daud et al. (2009); Tatsi et al. (2003); Amokrane et al. (1997) and Tchobanoglous et al. (1993) classified the two main groups of leachate as young or fresh leachate and mature or stabilized leachate.

At the early stage and within a short period of time, the landfill is in acidic phase and in aerobic condition. As the landfill ages, it shifts to a methanogenic phase in anaerobic condition, a process that usually takes a relatively longer period of time. In these two distinct phases, the characteristics of leachate differ. Table 2.3 shows the main characteristics of these two categories. The young leachate is referred to the one produced within less than five years while the mature leachate is referred to those produced after ten years.

Table 2.3: Characteristics of young (fresh) and mature (stabilized) leachate

Leachate Type	Young (Fresh)		**Mature (Stabilized)**	
Parameter	Mean	Range	Mean	Range
pH	6.2	4.9-6.7	7.9	7.3-8.8
BOD_5(mg/L)	26 800	9500-80 800	1050	50 – 4200
COD(mg/L)	5350	700-1500	70 900	44 000-115 000
NH_3-N (mg/L)	3100	1400-10 250	940	40-1750
Colour (PtCo)	10 550	6250-20 000	7600	950-15 150
Alkalinity (mg $CaCO_3$/L)	12 880	3540-26 200	4950	920-8070

Table 2.3: Continued

Leachate Type	Young (Fresh)		Mature (Stabilized)	
Parameter	Mean	Range	Mean	Range
Turbidity (NTU)	1700	1100-2700	340	75-1150
Conductivity (mS/cm)	29.5	23.0-35.5	18.3	6.2-34.0
BOD_5/COD	< 0.5		< 0.1	
Heavy Metal (mg/L)	< 2.0		< 2.0	

(Source: Tatsi et al., 2003; Cecen and Gursoy, 2000; Amokrane et al., 1997)

According to Garcia et al. (1996), young leachate is in acidic condition because of the presence of volatile fatty acids and salts such as acetate, propionate, and butyrate. Young leachate is also typically characterized by high BOD_5 and COD concentrations and a high ratio of BOD_5 to COD. This characteristic shows that a proportion of soluble organic materials are readily degradable. This reaction produces leachate with a pH of around 5 or 6. The presence of ammonia in high concentrations helps the other components of waste to dissolve. High concentrations of iron, manganese, zinc, calcium, and magnesium are also present in this stage (Irene and Lo, 1996). Young leachate is more polluted compared to mature or stabilized leachate (Tatsi et al., 2002).

In contrast, mature or stabilized leachates are usually highly contaminated with NH_3-N and have a moderately high COD strength. The pH of a mature leachate is higher than that of a young leachate because mature leachate is produced during or after methane fermentation. Hence, the pH of mature or stabilized leachate is higher than 7.5. As landfill ages, the biodegradable fraction of organic pollutants in leachate decreases as an outcome of the anaerobic decomposition that happens in landfill site, which contains more refractory organic matters than young leachate (Timur and

Ozturk, 1999). A significant proportion of recalcitrant materials (more than 60% of TOC) comprise humic substances, mainly humic acids (Artiola et al., 1982). These humic substances are natural organic matter made up of complex structures of polymerized organic acids, carboxylic acids, and carbohydrates (Amokrane et al., 1997, Tatsi et al., 2003).

2.4.3 Kuala Sepetang Landfill Site

Kuala Sepetang Landfill Site (KSLS) is situated at 4°49'30" N and 100° 40'44.08" E near the town of Taiping, Perak, Malaysia. According to the technical guidebook by Ministry of Housing and Local Government (MHLG), KSLS is designed as a level IV sanitary landfill. Despite meeting the level IV criteria, KSLS is still regarded as level I or an open dump site by Majlis Perbandaran Taiping (MPT).

KSLS is an old site that covers an area of 50.29 acres. Despite receiving EIA approval from DOE in 1994, the landfill site only began operations in 2001. The site is managed as an open dump and is being developed as a sanitary landfill. The access road to the landfill site is completely paved. The soil is only covered when necessary instead of daily as proposed in the MHLG technical guidebook. In terms of landfill operation, KSLS accepts municipal and commercial wastes from the surrounding areas of Taiping. The volume of these wastes reaches about 250 tons to 300 tons per day.

KSLS (Figure 2.7) currently has three phases. The now-closed Phase 1 covers an area of 4.89 acres. It neither has covered material for the wastes that are being

dumped nor a recirculation system for leachates. However, a liner system and gas vents are installed to the cell. The wastes are about 6 m high. The underlying material used for the liner has a permeability of less than 10^{-7} m/s. Geotextile T40 and used tires are selected as liners in this phase. Phase 2 fully utilizes an area of 4.38 acres. Unfortunately, this phase is badly polluted because no engineered containments or liner systems are installed.

Therefore, the operations in this phase have been terminated as the wastes have reached 8 m high. Phase 3 covers 4.96 acres of fully developed cells that are complete with liners, leachate collection systems, and gas venting systems. This phase has already reached its peak with a 5 m waste height.

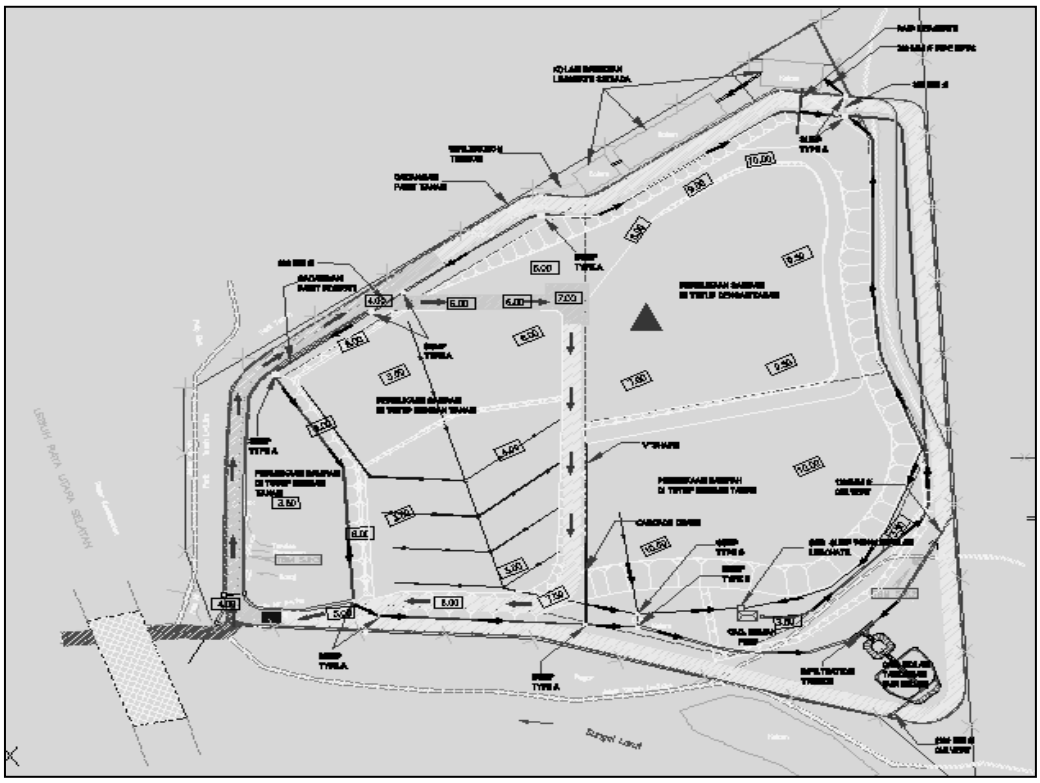

Figure 2.7: Locations of Phase 1, 2, and 3 in Kuala Sepetang landfill (Source: Majlis Perbandaran Taiping, 2012)

Several studies have been carried out to treat leachate from this landfill. Some main parameters, such as BOD, COD, NH_3-N, colour, and turbidity, were selected as indicators to measure the effectiveness of the treatment. The types of treatment that have been studied include PAC-augmented SBR (Aziz, 2011), chlorine disinfection (Umar et al., 2011), and a combination of activated carbon and zeolite (Abu foul, 2007). Table 2.4 shows the characteristics of raw leachate from KSLS based on previous studies. Leachates produced in this site have low BOD_5/COD and high concentrations of COD and NH_3-N (Aziz et al., 2010).

Table 2.4: Characteristics of raw leachate at Kuala Sepetang landfill

Parameter	Unit	Aziz et al., 2010	Umar et al., 2010
pH	-	8.66	8.1
Colour	Pt Co	6398	-
Suspended solids	mg/L	693	-
BOD_5	mg/L	257	85
COD	mg/L	1456	990
BOD_5/COD	-	0.19	0.09
NH_3-N	mg/L	564	996
Total iron	mg/L	3.43	5
Zinc	mg/L	0.22	0.2

2.4.4 Kulim Landfill Site

KLS is located at PT 9535, Lot 8724 in Mukim Padang Cina, District of Kulim, with geographical coordinates of 5°25'0" N and 100°37'0" E (Figure 2.8). This site can be reached through Jalan Kilang Lama-Karangan. KLS is located 5 km from Kulim Hi-Tech Park and 14 km from Kulim town. The entire landfill site

covers an area of 56.7 ha, of which 9.7 ha is presently operational. KLS operations officially commenced in 1996. According to a Majlis Perbandaran Kulim Kedah (MPKK) officer, KLS is regarded as a level II covered sanitary landfill. The access road to the landfill site is completely paved. It receives approximately 300 tons of MWS daily.

The produced leachates are transported to a lined collection pond, where they remain for a specific retention time, through a HDPE pipe with a 30 cm diameter. However, the leachates are not treated after this stage. The values obtained by researchers who studied the characteristics of landfill leachate at KLS are depicted in Table 2.5. The leachate is considered as low biodegradable with high concentrations of COD and NH_3-N (Aziz et al., 2010; Umar et al., 2010).

Table 2.5: Characteristics of Kulim landfill leachate

Parameter	Unit	Aziz et al., 2010	Umar et al., 2010
pH	-	8.02	7.8
Colour	Pt Co	3029	-
Suspended solids	mg/L	553	-
BOD_5	mg/L	285	515
COD	mg/L	1295	1593
BOD_5/COD	-	0.2	0.32
NH_3-N	mg/L	562	503
Total iron	mg/L	3.82	6
Zinc	mg/L	0.33	0.3

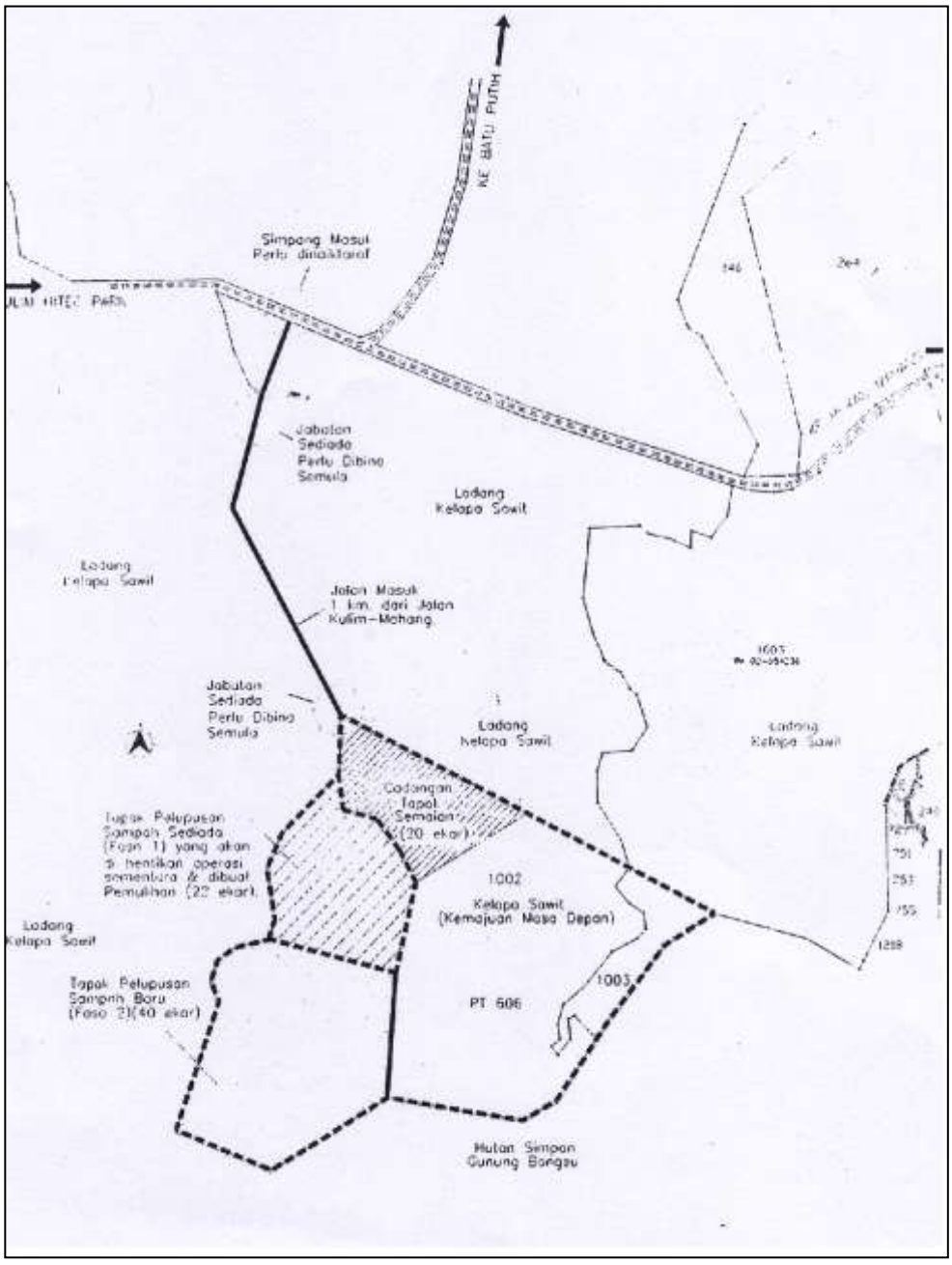

Figure 2.8: Kulim landfill area location (Source: Majlis Perbandaran Kulim Kedah, 2012)

2.5 Leachate Treatment Technology

Landfill leachate, a highly polluted industrial wastewater, has been a cause for significant concern because landfilling is the most common technique for solid waste disposal (Ghafari et al., 2005). The discharge of landfill leachate can lead to serious environmental problems as it may percolate through the soil and subsoil, causing extensive pollution of ground and surface waters if not properly treated and safely disposed. Hence, leachate needs to be specially treated before being discharged to the surrounding environment.

Various studies have been carried out to remove as much undesirable constituents from landfill leachate as possible. Rivas et al. (2004) stated that leachate treatment technologies can be classified into biological treatment and physical and chemical methods.

2.5.1 Biological treatment

Biological treatment is the most common practice for leachate treatment, which is relatively economical compared to physicochemical methods. The process can involve aerobic or anaerobic treatment. Under aerobic conditions, biological treatment uses microorganisms that can degrade organic compounds to CO_2 and sludge. However, the degraded organic compounds will generate biogas under an anaerobic environment. This treatment is effective for the removal of young leachate containing high concentrations of volatile fatty acid (Tatsi et al., 2003). It is not effective for the removal of stabilized leachate (Amokrane et al., 1997) because this contains humic acid, which is difficult to process further using biological means.

2.5.1.1 Aerobic Treatment

In aerobic treatment, organic contaminants are mostly transformed into CO_2 and sludge using the atmospheric O_2 that is transferred to the wastewater. This type of treatment can readily reduce the high organic load present in leachate during the early stages of waste decomposition (Salem et al., 2008). The most common aerobic treatments are aerated lagoon, sequencing batch reactor (SBR), and activated sludge (Li and Zhao, 2001; Lin and Chang, 2000; Bae et al., 1999).

2.5.1.2 Anaerobic Treatment

The anaerobic method of leachate treatment involves microorganisms that can live in oxygen-deprived conditions. These microorganisms convert organic material to CO_2, methane, and other metabolic products. Anaerobic treatment involves two stages. The first stage is acid fermentation, where the facultative and anaerobic bacteria break down complex organics into simple substances, such as acetic acid or other acids of low molecular weight. In the second stage, methanogenic bacteria form methane and CO_2 from organic acids (Crawford and Smith, 1985). Examples of anaerobic processes are conventional anaerobic digester, anaerobic activated sludge, and anaerobic filter.

2.5.2 Physical and Chemical Treatment

Stabilized leachates are characterized by ammonia, refractory substances, and low biodegradable organic fraction ($BOD_5/COD < 0.1$). Therefore, stabilized

leachates cannot be treated to the required standards using biological processes alone. Physical and chemical treatments for landfill leachate are also used in addition to the treatment line, such as in pre-treatment or in the last purification process. However, some treatment methods are only suitable to treat specific pollutants, such as stripping for ammonia.

2.5.2.1 Flotation

Flotation is extensively used and is focused on the reduction of colloids, ions, macromolecules, microorganisms, and fibers. Very few studies have been conducted with regard to the application of flotation for the treatment of landfill leachate. Zouboulis et al. (2003) investigated the use of a flotation column as a post-treatment step to remove residual humic acids from simulated leachate. Under optimized conditions, the researchers removed about 60% of the humic acids. Adlan et al. (2011) and Palaniandy et al. (2010) examined the use of a dissolved air flotation (DAF) process for the treatment of landfill leachate in the presence and absence of a coagulation process. According to the results of Palaniandy et al. (2010), the removal efficiencies of colour, COD, and turbidity from leachate using DAF without the coagulation process were 36%, 33%, and 32%, respectively, whereas the removal efficiencies with the coagulation process were 70%, 79%, and 42%, respectively.

2.5.2.2 Adsorption

Adsorption is the accumulation of a substance at the interface between two phases. The material adsorbed is called the adsorbate or solute, and the adsorbing phase is the adsorbent. The principal types of adsorbents include activated carbon and synthetic-, polymer-, and silica-based adsorbents. Activated carbon is commonly used in advanced wastewater application because the high cost of synthetic-, polymer-, and silica-based adsorbents hinders their widespread use. The adsorption of pollutants onto the activated carbon in columns or in powder form provides better reduction in COD levels than the chemical methods (Kargi and Pamukoglu, 2003; Fettig et al., 1996). Adsorption by activated carbon is used as a polishing or final treatment to enhance treatment quality.

Rodriguez et al. (2004) studied the efficiency of powdered activated carbon (PAC) and different resins in the reduction of non-biodegradable organic matter from landfill leachate. However, activated carbon presented the highest adsorption capacities with an 85% decrease in COD and a residual COD of 200 mg/L. Although the adsorption process can provide a high removal rate for non-biodegradable organic matter, the main problem for this process is the need for frequent regeneration of columns or the high consumption of PAC, which is needed to maintain and enhance the adsorption process.

2.5.2.3 Air Stripping

Air stripping involves the mass transfer of a gas from the liquid phase to the gas phase. The transfer is accomplished by allowing the liquid, which contains the gas to be stripped, to come in contact with the air that does not contain the gas initially. The removal of dissolved gases from wastewater using air stripping has received considerable attention, especially for the removal of ammonia. High levels of NH_3-N are usually found in landfill leachate and can increase wastewater toxicity. Air stripping can therefore be successful in eliminating this pollutant (Marttinen et al., 2002). For this method, high pH values must be applied so the column can work efficiently (Hao et al., 2010; Ozturk et al., 2003; Marttinen et al., 2002).

Compared to other treatment techniques such as reverse osmosis and nanofiltration, ammonium stripping is discovered to be more economical in terms of operational costs. Regardless of its advantages, the major concern about ammonia air stripping is the release of NH_3 into the atmosphere. If ammonia cannot be properly absorbed by either H_2SO_4 or HCI, its emission can cause severe air pollution. Another disadvantage of this technique is the scaling of calcium carbonate in the stripping tower when lime is used to adjust pH (Li et al., 1999).

2.6 Coagulation

2.6.1 General Overview

Coagulation is a conventional process commonly used in water and wastewater treatment. Generally, it is often coupled with other processes like flocculation, biological process, oxidation or filtration to achieve desirable effluent quality (Guo et al., 2010; Maranon et al., 2008; Mariam and Nghiem, 2010; Wu et al., 2010).

The jar test is the most widely used method for evaluating and optimizing the coagulation-flocculation process (Al-Dawery and Joubori, 2012; Ghafari et al., 2010; Matilainen et al., 2010; Davis and Cornwell, 2008; Mishra and Bajpai, 2006; Ndabigengesere and Narasiah, 1998). The general approach for this method involves pH adjustment and the addition of coagulants to wastewater to overcome the repulsive forces between the particles (Matilainen et al., 2010; Duan and Gregory, 2003; Ayoub et al., 2001). Jar tests are widely used to determine the effects of solution pH, coagulant dose, mixing speed (rpm), settling time, and other variables on the removal of solids from water or wastewater (Peavey et al., 1985; Davis and Cornwell, 2008). The interpretation of test results involves visual and chemical testing of the treated water (Al-Dawery and Joubori, 2012).

Generally, coagulation followed by flocculation is applied to assist in the removal of suspended and colloidal particles from a solution. This process, which is usually done in sequence, is a combination of physical and chemical procedures.

2.6.2 Definition of Coagulation Process

Coagulation is defined as the process in which chemicals or so-called coagulants are added to reduce repelling forces between colloidal particles that keep them in stable state, and induce attraction between colloidal particles to form agglomerates (Letterman et al., 1999). Basically, coagulation is described as the process of decreasing or neutralizing the negative charge of suspended particles, where cationic coagulants provide positive electric charges to neutralize the negative charges of the colloids.

As a result, the particles collide to form larger particles (flocs). In this process, rapid mixing is allowed to disperse the coagulant, promote particle collisions, and maximize the effectiveness of the process. This task must be done carefully so that the solution will not have an overdose of coagulants that can cause a complete charge reversal and restabilize the colloidal complex. The coagulation mechanism is shown in Figure 2.9.

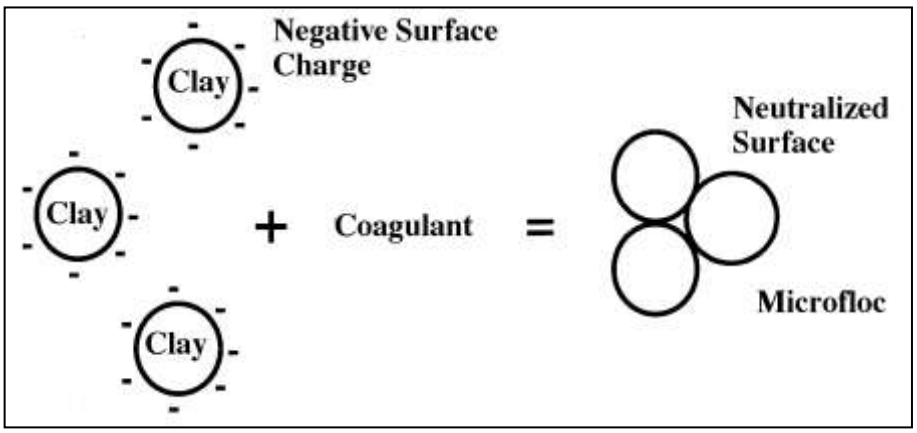

Figure 2.9: Coagulation of fine clay particles in slurry (Source: Pillai, 1997)

2.7 Flocculation

Owing to the increase in particle size, coagulation is usually followed by the flocculation of unstable particles into bulky flocs so they can settle easier (Cheng et al., 1994). Flocculation is the action of polymers that form bridges between flocs to bind the particles into large agglomerates or clumps. Figure 2.10 shows the mechanism of flocculation on fine clay particles.

Bridging can occur when segments of the polymer chain adsorbed on different particles and help them aggregate. High molecular weight polymers called coagulant aids may be added during this step to help bridge, bind, and strengthen the floc; add to its weight; and increase its settling rate (Natalia and Olli, 2006; Somasundaran et al., 2005).

During flocculation, slow stirring or gentle agitation is required to allow contact between the small flocs, agglomerate them into larger flocs, and enhance subsequent removal. These large flocs can be removed using a solid removal process, such as sedimentation, rapid or membrane filtration, or DAF (Dempsey, 2006; Letterman et al., 1999).

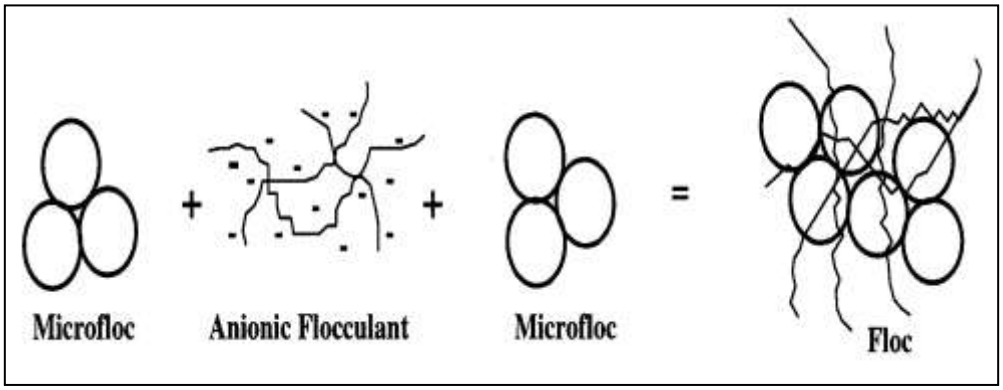

Figure 2.10: Flocculation of coagulated fine clay particles (Source: Pillai, 1997)

2.8 Introduction to Colloids

It is essential to understand the significance of colloids in landfill leachate and the basic colloidal science concepts before discussing their coagulation mechanism.

2.8.1 Colloids in Landfill Leachate

Landfill leachate contains of non-sedimentary suspending materials with negligible settling velocity; and colloids are the major constituents of these particles. Colloids are generally defined as solid particles within the size between 1 nm and 1 mm (IUPAC, 2010: Christian et al., 2008; Wigginton, Haus and Hochella, 2007). Colloids are not visible under an ordinary microscope (Hammer and Mark, 2004).

However, they can be seen as specks of light with an ultra microscope when a beam of light is passed through the suspension. This is due to the Tyndall effect, which is the scattering of lights by colloidal particles (Barnes et al., 1986).

Matura and co-workers had mentioned that colloidal particulates in landfill leachate were mostly inorganic, mainly composed of carbonates and clays (Matura, Etler and Klementovà, 2011; Matura et al., 2010). In addition, colloids can be classified as hydrophobic and hydrophilic. Hydro- refers to the water phase where the colloids exist while –phobic and –philic refers to the degree of affinity for the liquid phase by the colloids (Bratby, 2006). Hydrophobic infers water repellence which is dependent on electrical charge or mutual repulsion for its stability in suspension (Hammer and Mark, 2004; Barnes et al., 1986). Hydrophilic infers a

strong affinity for water molecules in the surfaces layers of the colloids to stay in stability because of the slight charge that they might posses (Bratby, 2006; Hammer and Mark, 2004)

2.8.2 Colloidal Stability

Stability refers to the ability of particles to remain as separate entities or in a dispersion state for long periods rather than form aggregates (Gregory and Duan, 2001). Most colloidal particles in wastewater have a negative charge in nature (Koohestanian et al., 2008). Their colloidal dispersions are stabilized because of the electrostatic repulsion between adjacent particles, which usually overwhelm the attractive van der Waals force and prevent particle aggregation.

Since colloids have a high surface area to weight ratio, they are hard to be removed by gravity or sedimentation.This phenomenon implies that the effective removal of colloidal dispersions is highly influenced by its electrokinetic properties. Colloid electrokinetic properties are commonly illustrated by the electrical double-layer model and the theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO) in Sections 2.8.2.1 and 2.8.2.2.

2.8.2.1 Electrical Double Layer Model

The combined Gouy–Chapman–Stern model is the most commonly used double-layer model, which plays a fundamental role in the mechanism of the electrostatic stabilization of colloids. The double-layer model explains the ionic environment and the setup of repulsive forces that surround a charged colloid.

A single, negatively charged colloid will initially attract some of the positive ions (or counterions) in the solution to form a firmly attached layer, known as the Stern layer, around the surface of the colloid. Additional positive ions are still attracted to the negative colloid, but they are also repelled by the Stern layer and by the other positively charged ions attempting to get close to the negatively charged colloid.

This constant attraction and repulsion results in the formation of a diffuse layer of charged ions that surrounds the colloid and the Stern layer. The diffuse layer can be visualized as a charged atmosphere that surrounds the colloid. The attached positively charged ions in the Stern layer and the charged atmosphere in the diffuse layer is together referred as the double layer. The charge is a maximum at the particle surface and decreases with distance from the surface. The thickness of this layer depends on the type and concentration of ions in the solution.

The Stern layer is considered to be rigidly attached to the colloid while the diffused layer is a dynamic layer of charged particles. Nerst Potential is the voltage measurement (in millivolts) in the diffuse layer. The potential is at its maximum at the Stern layer and drops exponentially through the diffuse layer. Zeta potential is the electrical potential that represents the difference in voltage between the surface of the diffused layer and the dispersant (Figure 2.11). Knowing the magnitude of the zeta potential is essential because it represents the strength of the repulsion between colloidal particles and the distance that must be overcome to bring the particles together.

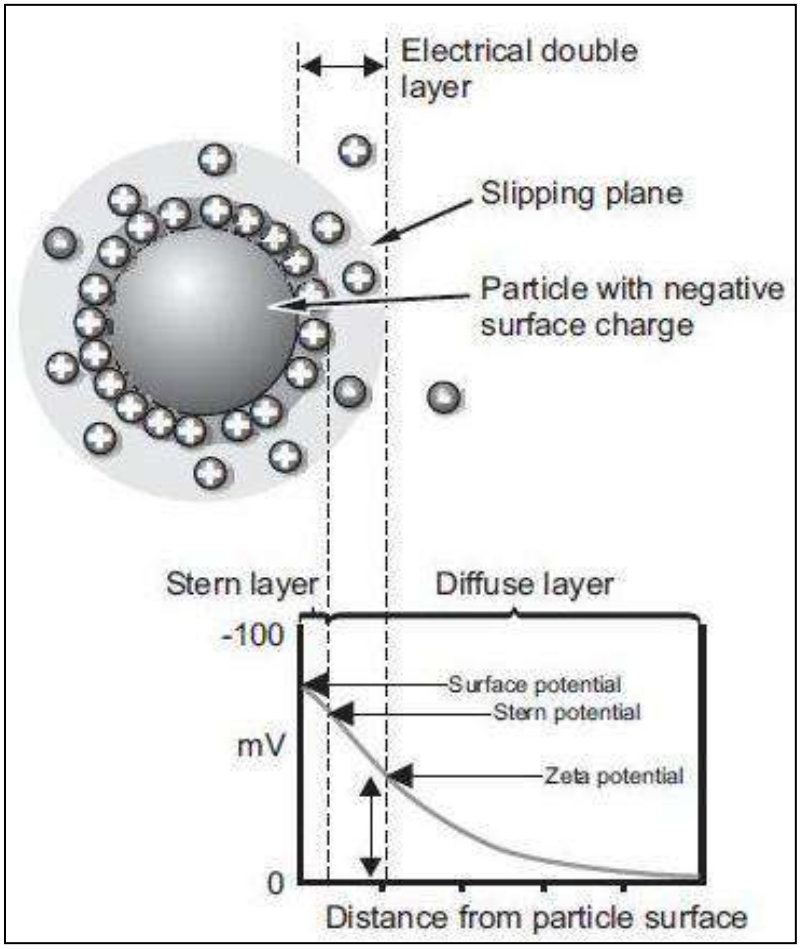

Figure 2.11: Schematic representation of Zeta Potential (Source: Zetasizer Nano User Manual, 2008)

Since double layer electrokinetic quantification by Stern potential measurement is difficult and laborious, zeta potential would be an adequate substitute (Cosgrove, 2010; Bratby, 2006; Norde, 2003). Zeta potential is very dependent on pH and the pH for which zeta potential is zero, is defined as isoelectric point (IEP) or point of zero charge (PZC) (Kaszuba et al., 2010; Ravina, 2006). Both Sympatec GmbH (2009) and Shammas (2005) had illustrated colloid stability level (Tabble 2.6) and coagulation degree (Table 2.7) respectively based on zeta potential.

Table 2.6: Degree of colloid stability as a function of zeta potential

Zeta potential (mV)	Colloid stability
from 0 to ±5	Rapid coagulation or flocculation
from ±10 to ±30	Incipient stability
from ±30 to ±40	Moderate stability
from ±40 to ±60	Good stability
more than ±61	Excellent stability

(Source: Sympatec GmbH, 2009)

Table 2.7: Degree of coagulation as a function of zeta potential

Zeta potential (mV)	Degree of coagulation
from +3 to 0	Maximum
from -1 to -4	Excellent
from -5 to -10	Fair
from -11 to -20	Poor
from -21 to -30	Virtually none

(Source: Shammas, 2005)

According to Table 2.6 and 2.7, the magnitude of the zeta potential indicates the potential stability of a colloidal system. If all the particles in a suspension have a large negative or positive zeta potential, then they will tend to repel each other and no tendency for the particles to come together will occur. However, if the particles have low zeta potential values, then no force will prevent the particles from coming together and flocculating. As this electric potential approaches zero, particles tend to aggregate. Therefore, a lower zeta potential means a more effective coagulation.

Nevertheless, there are other coagulation mechanisms than charge destabilization which will be discussed in Section 2.14. Hence, indication of coagulation performance by zeta potential is only appropriate if charge destabilization is the predominant coagulation mechanism (Bratby, 2006). Deviation of zeta potential from zero to optimum coagulation conditions indicates other coagulation mechanisms surmount the coagulation process, not charge neutralization (Eikebrokk, Juhna and Østerhus, 2006).

2.8.2.2 DLVO Theory

Developed in the 1940s, DLVO theory deals with the stability of colloidal systems. According to DLVO theory, colloidal stability can be predicted by considering van der Waals and electrical double layer interactions. It calculates the balance of two opposing forces between charged colloidal particles, namely van der Waals attraction (attraction forces) and electrostatic repulsion (repulsive forces) (Binks and Horozov, 2006; Pashley and Karaman, 2004; Gregory and Duan, 2001). Prediction of this model is in line with the Schulze-Hardy rule, which emphasizes the dependence of colloid stability or coagulations on the added electrolyte's concentration and valency (Tadros, 2007; Shammas 2005).

In water, colloidal particles collide with water molecules constantly and randomly, termed as Brownian movement. As particles with similar charges approach one another, the repulsive electrostatic forces increase to keep them separated. However, if they can neutralize the electrokinetic potential, then the attractive van der Waals force will dominate and the particles will remain close

together, forming larger flocs (in agreement with aforementioned zeta potential concept). In this case, coagulant can be introduced into the wastewater to do the trick.

2.9 Coagulants

Coagulants are chemicals added into water or wastewater to perform coagulation. According to Figure 2.12, there are two general categories of materials used in the coagulation process: metal coagulants (e.g. aluminum sulphate, polyaluminum chloride, and ferric chloride), naturally occurring coagulants (e.g. chitosan and plant extracts) or synthetic polymer (e.g. polyacrylamide derivatives and polyethylene imine). These coagulants are used to enhance solid/liquid separation by aggregating fine particles into large agglomerates, producing entities that are faster to settle and easier to capture in filters (Gray and Ritchie, 2006).

Shammas (2005) stated the general requirements for coagulants in water treatment are: (i) trivalent metallic cations or polymers that have been proven efficient as coagulants; (ii) nontoxic and do not cause any detrimental physiological effects on human health; and (iii) insoluble or low solubility in the pH ranges common in water treatment. Coagulant for the particular wastewater has to be selected carefully based on their feasibilities. This is necessary in order to have an efficient coagulation process and to be able to leave the lowest possible residual of the chemical in the treated water.

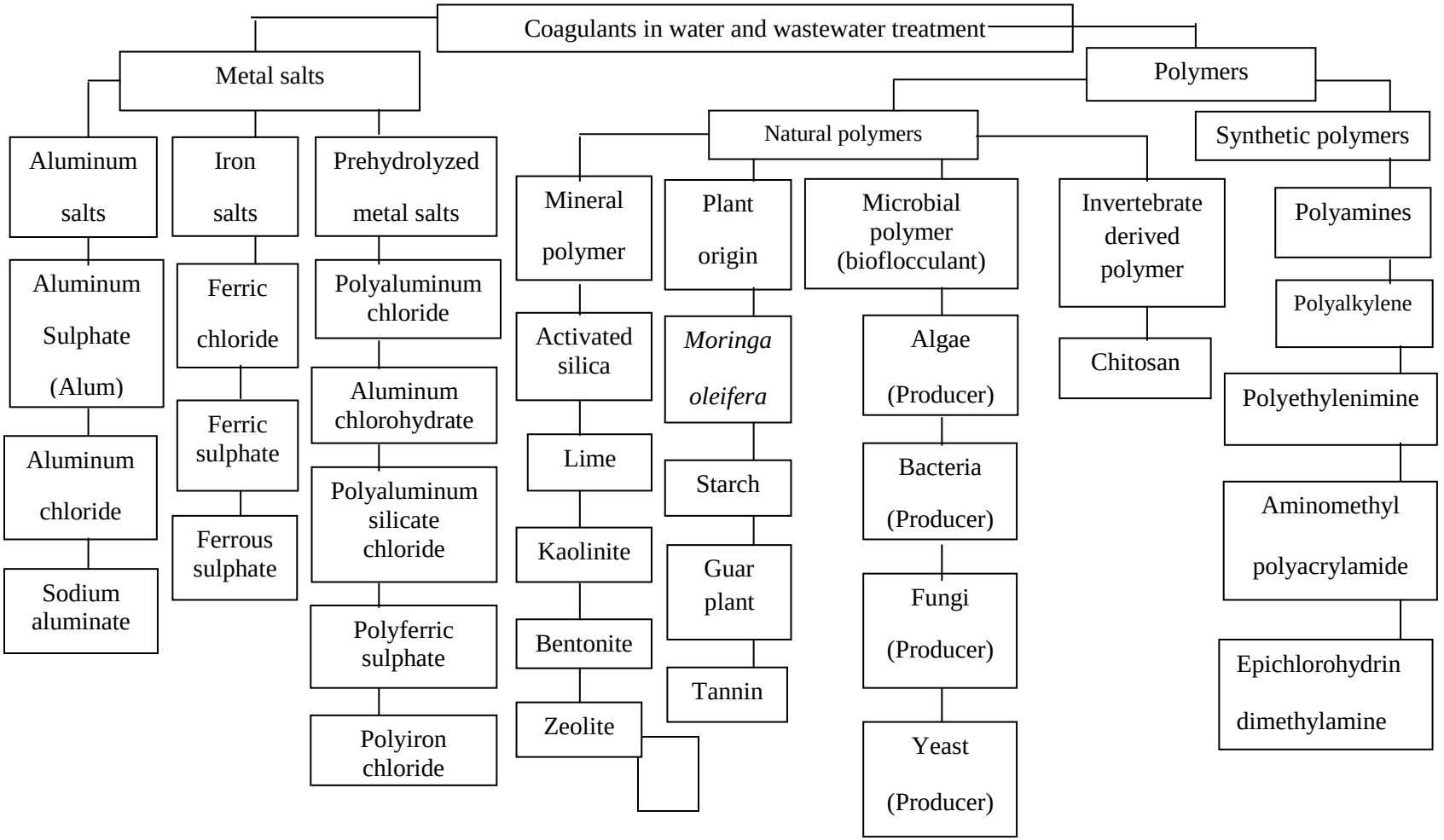

Figure 2.12: Classification of coagulants in water and wastewater treatment (Source: Bratby, 2006)

2.9.1 Metal Coagulants

The two main classifications of metal coagulants (inorganic) are aluminum and iron based. The most common aluminum-based coagulants include aluminum sulfate (generally known as alum), aluminum chloride, and sodium aluminate. Iron-based coagulants include ferric sulfate, ferrous sulfate, ferric chloride, and ferric chloride sulfate. Aside from these, other chemicals such as hydrated lime and magnesium carbonate were also used as coagulants (Letterman et al., 1999).

The effectiveness of these coagulants arises principally from their ability to form multi-charged polynuclear complexes with enhanced adsorption characteristics. When metal coagulants are added into water, the metal ions (Al and Fe) hydrolyze rapidly and uncontrollably and form a series of metal hydrolysis species. The efficiency of rapid mixing, the pH, and the coagulant dosage determine the hydrolysis species that is effective for treatment (Bratby, 2006; Jiang and Graham, 1998).

Numerous studies have shown that iron-based coagulants are often more efficient than aluminum ones (Zazouli and Yousefi, 2008; Aziz et al., 2007b; Aboulhassan et al., 2006; Niquette et al., 2004; Douglas et al., 1998; Reynolds and Richards, 1996; Tillman, 1996). This efficiency is attributed to the wider effective pH range of iron-based coagulants compared to that of aluminum-based coagulants. For example, Reynolds and Richards (1996) stated that the optimum pH of ferric chloride is between pH 4 and pH 12, while Tillman (1996) mentioned that the appropriate pH for ferric chloride is between pH 4 and pH 11. However, the

optimum pH for alum reaction was found to be between pH 4 and pH 8 (Reynolds and Richards, 1996).

Aziz et al. (2007b) investigated the effectiveness of alum, ferric chloride, ferrous sulfate, and ferric sulfate in the removal of colour from a leachate sample at different pH conditions, pH 4, pH 6, and pH 12. Results showed that 800 mg/L of ferric chloride (pH 4) managed to remove 94% of the colour compared to 2200 mg/L alum (pH 4) with an 82% colour removal rate. Besides having a wider pH range compared to aluminum, iron-based coagulants require a lower effective dosage to reach the exact removal percentage achieved by aluminum (Duan and Gregory, 2003). A good example was reported by Zazouli and Yousefi (2008) when only 1000 mg/L ferric chloride (pH 10) was needed to achieve 28% of COD removal compared to 1400 mg/L alum (pH 6.5), which gave only 21% COD removal from a young leachate sample.

Other aluminum based coagulants that are applied in coagulation process are polyaluminum chloride (PACI). This compound used widely in water and wastewater treatment especially in China, Japan, Russia, and Western Europe (Ghafari et al., 2009; Sinha et al., 2004; Amirtharajah and O'Melia, 1990). PACI chemistry is similar to that of alum, except that PACI contains highly charged polymeric aluminum species and also known as inorganic polymeric coagulants. Researchers have demonstrated that the tridecameric Al_{13} species with the formula $Al_{13}O_4(OH)_{24}^{7+}$ (abbreviated as Al_{13}^{7+}) is the most active species for coagulation in PACl (Zhao et al., 2009; Pernitsky and Edzwald, 2006; Gao et al., 2005; Gregory and Duan, 2001).

This compound also makes the charge density of PACI higher. Another important characteristic in PACI is the relative basicity, expressed as a percentage. Relative basicity is the molar ratio of negative to positive charges of the compound. For example, in PACI, it has a total of (13 x 3 = 39 positive charges) and (4 x 2 + 24 x 1 = 32 negative charges). Thus, the relative basicity of this compound is (32/39) x 100 = 82 %.

Their significant advantage is in the way their hydrolysis occurs under specific experimental conditions during the preparation stage of the coagulants and not after their addition to the raw solution. PACI is known to provide better coagulation than alum at low temperatures and produce lower volumes of sludge but are quite expensive compared to metal salts. It has less dependence on the pH of the water, which reduces the need for pH correction because it is already partially neutralized (Renault et al., 2009; Duan and Gregory, 2003).

2.9.2 Polymeric Coagulants

Polymers are composed of a wide range of natural or synthetic, water-soluble, and macromolecular compounds that have the ability to destabilize in the coagulation–flocculation process.

Polyelectrolytes are polymers with ionizable functional groups such as carboxyl, amino or sulphonic groups.They are commercially available in cationic (with positive functional groups), anionic (with hegative functional groups) or

amphoteric (with both positive and negative functional groups). Polymers without any ionizable functional group are nonionic.

Polyelectrolytes are high molecular weight polymers which contain adsorbable groups and form bridges between particles or charged flocs to form larger, stronger , higher density and good compacting flocs for easier settling (Ozkan and Yekeler, 2004). These mechanisms are elaborated in Section 2.14.

Polymers are effective over a wider pH range compared to metal coagulants. They can be applied at lower doses and do not consume alkalinity. Polyelectrolytes are high molecular weight . The greater the molecular weight causes the greater the chain length and also flocculating ability. Longer chain length allows bridging, or attaching to, greater numbers of particles.

Furthermore, the use of polyelectroltes especially those of high molecular weight has resulted in tremendous performance improvement for separation process. The use of polymers produces smaller volumes of clarification sludge than the use of metallic coagulants (Ndabigengesere et al., 1995). A brief comparison of these typical polymeric coagulants is presented in Table 2.8.

Table 2.8: Comparisons of coagulants in water and wastewater treatment

Coagulant class & chemicals	Advantages	Disadvantages	References
Aluminum salts -Alum -Aluminum chloride -Sodium aluminate	-Low cost; -High efficiency at low dose; -Most commonly used; -Relatively high availability; -Attracts inorganic suspended solids effectively; -Easy to handle and apply; -Produce less sludge than lime.	-Typically requiring alkaline additives to achieve optimum pH; -Effective over a limited pH range; -Fast mixing is critical to proper functioning; -Non optimal pH leads to excessive dosage requirements; -Should be used between pH 5.5 and 7.5; -Performance substantially degrades at lower temperatures; -Poor efficiency for attracting organic suspended solids; -Relatively large dosage required when used alone; -Flocs formed from alum at low temperatures settle very slowly; -Possible reaction relation to neurological disorders (e.g. Alzheimer's disease) and other similar health related problems associated with residual aluminum concentrations in treated water.	Rui et al., 2012; Apostol et al., 2011; R&D, 2010; Niquette et al., 2004 Flaten, 2001; Schulz and Okun, 1984

Table 2.8: Continued

Coagulant class & chemicals	Advantages	Disadvantages	References
Iron salts -Ferric chloride -Ferric sulphate -Ferrous sulphate	-Alternative to alum; -Gives more compact sludge; -Works well within all temperature range; -Best removal for organic compounds; -pH sensitivity is somewhat less than alum; -Suitable for usage in the lime softening process (pH 9)	-Lower efficiency for removing organic suspended solids than alum; -Fast mixing is critical to proper functioning; should be used between pH 5.5-8.5; -Typically requiring alkaline additives to achieve optimum pH; -Generally large dosage required; -Improper doses cause reddish colour and high iron residual; -High iron residual can plug filters and stain laundry; -Aesthetically unpleasing sludge (brown).	Rui et al., 2012; R&D, 2010; Niquette et al., 2004 Schulz and Okun, 1984

Table 2.8: Continued

Coagulant class & chemicals	Advantages	Disadvantages	References
Prehydrolyzed metal salts -Polyaluminum chloride (PACI/PAC) -Aluminum chlorohydrate -Polyaluminum sulphate chloride -Polyaluminum silicate chloride -Polyferric sulphate -Polyiron chloride	-Work well at low raw water temperatures; -Less sludge is produced compared to alum at an equivalent dosage; -Does not require addition of alkali to raw water for coagulation; -Much less sensitive to pH, effective over wider range of pH (pH 4.5 – 9.5) than alum; -Mixing time not critical; -Floc formed is more dense and faster settling than alum;	-Not commonly used; -Little full scale data compared to other aluminum based coagulants; -Generally requires an onsite production process to prepare pre hydrolyzed metallic salts than alum or ferric chloride.	R&D, 2010; Zouboulis and Tzoupanos, 2010; Gebbie, 2001

Table 2.8: Continued

Coagulant class & chemicals	Advantages	Disadvantages	References
Synthetic cationic polymers -Epichlorohydrin dimethylamine -Polyamines -Polyalkylene -Polyethylenimine -Aminomethyl polyacrylamide	-Lower dosages required; -Producing denser sludge when used in combination with metal salts; -Greatly reduces their dosage requirement resulting in economic benefits.	Determining correct proportion for mixing with inorganic coagulants and other additives has been challenging due to a historical lack of instrumentation for determining relative amounts of inorganic, organic and biological suspended solids in raw water.	R&D, 2010; Bolto and Gregory, 2007; Nozaic et al., 2001

Table 2.8: Continued

Coagulant class & chemicals	Advantages	Disadvantages	References
Natural polymers -*Moringa oleifera* -Starch -Chitosan, -Guar plant -Tannin -Tamarind tree -Red Sorella plant -Fenugreek -Sodium alginate	-Biodegradable; -Less contamination risk of toxic or detrimental residuals like aluminium and acrylamide; -Often locally available and less expensive; -Requires lower dosages, typically 1/10 to 1/5 of those for metallic salts; -Often produces less sludge as lower dosages are used, thus requires simplier sludge handling facilities; -Less pH sensitive and is effective over a wide pH range, unlike metallic salts; -Does not increase dissolved solids content of water significantly.	-May not always be effective and requires case-by-case assessment; -Often less effective compared to metallic coagulant; -Often more effective as coagulant aid in conjunction with metallic coagulant, at typical dosages of 2-20 mg/L; -May be inappropriate for large scale treatment and the extreme conditions (pH and concentration) of the wastewaters.	Vijayaraghavan et al., 2011; R&D, 2010; Yin, 2010; Niquette et al., 2004; Schulz and Okun, 1984

2.10 Coagulant Aids

The coagulation process is not always perfect. It may result in small flocs when the process takes place at low temperatures or in fragile flocs that break up when subjected to physical forces. Thus, several products known as coagulant aids can be used to achieve optimum conditions for coagulation process. The aim is to obtain faster floc formation, produce denser and stronger flocs, decrease the coagulant dosage, broaden the effective pH band and improve the removal of turbidity and other impurities (R&D, 2010; Bratby, 2006; Shammas, 2005).

Shammas (2005) stated that coagulant aids include four typical types, which are alkalinity addition, pH adjustment, particulate addition and polymers. A comparison of these coagulant aids with their classifications is summarized in Table 2.9. Coagulant aids can be classified according to their ionization traits, which include anions, cations, and amphoteric (with dual charges) ions.

The most commonly used coagulant aids are polyelectrolytes, especially those synthetic polymers like polyacrylamides and polydiallyl dimethyl ammonium chloride (poly-DADMAC) and polystyrene sulfonate. As seen in the Table 2.9, positively charged (cationic) polymers may be use in combination with aluminum- or iron-based coagulants to attract the SS and neutralize their surface charge (AWWA and ASCE, 1990). Their performances depend on the function of the product used and the characteristics of the raw water (Niquette et al., 2004).

Awang and Aziz (2012) tested the potential of using *Hibiscus rosa-sinensis* leaf extract in treating landfill leachate. This natural coagulant was found to act as coagulant aid in treating landfill leachate. At optimum dose of 4000 mg/L alum combined with 500 mg/L *Hibiscus rosa-sinensis* leaf extract effectively removed 100 % Fe^{3+} , 72 % SS and 60 % turbidity as compared with the use of 4000 mg/L alum alone (60, 45 and 36 % removals, respectively).

Al-Hamadani et al., (2011) studied the removal efficiency of COD, colour and TSS in landfill leachate by using psyllium husk as coagulant aid in the presence of PACI and alum as the main coagulants. It was observed that, psyllium husk was found to be more effective as coagulant aid with PACI in the removal of studied parameters as compared to alum. The maximum removal of efficiencies of COD, colour and TSS were 64, 90 and 96%, respectively.

A research based on *Cassia angustifolia* seed gum as a coagulant aid for the decolorization of different dye solutions has been carried out by Sanghi et al. (2002). In his findings, 1.5 mL dosage of *C. angustifolia* was added in conjunction with PACI (0.1 mL) enhanced colour removal from 47% to 70% and 67% to 83% for Acid Sandolan Red RSNI dyes and Direct Kahi Green dyes respectively. They concluded that *C. angustifolia* seed gum can act as working substitute, partially or fully for synthetic chemical coagulants such as PACI.

Sanghi et al. (2006) then extended their research on another species of the genus *Cassia*, namely, *Cassia javahikai* seed gum for the decolorization of textile dye solutions. *C. javahikai* seed gum was found to be a good working substitute as a

coagulant aid in conjunction with PACI in varying ratios, where it managed to decolorize all the dyes to more than 70% at a very low PACI dosage.

Polymers may be processed from various sources of starch, including potato, corn, cassava, arrowroot, and yams (Bratby, 2006). Starch is basically a highly polymerized carbohydrate. According to Omar et al. (2008), starch is a natural polymer that is categorized as a polyelectrolyte and can act as a coagulant aid. In addition, Aziz et al. (2000) performed an experiment by using sago (*Metroxylon spp*) as an alternative coagulant aid to remove heavy metals and turbidity in synthetic water. They also claimed that sago starch carries a negative charge. For an alum concentration of 25 mg/L at a pH value of 7.5, the removal of Zn improved by approximately 50% in the presence of 0.1 mg/L sago starch compared to the 24% improvement in the presence of alum alone. These experiments generally showed an improved removal of metals, except for turbidity, in the presence of sago starch.

The coagulant aids must be added in slow mixing condition in order to avoid breakage during their growth (Allegre et al., 2004). Aggregation of suspended solids by coagulant aids can be achieved in two mechanisms:

(i) Charge neutralization – direct reduction of surface charge on the particles by polymers.

(ii) Polymer bridging – adsorption of polymers on the surface of two or more suspended particles and thus joining them together in the form of a network.

Generally, a major use of natural polymers in water treatment as a coagulant aid to bridge the coagulated particles formed when aluminum or iron salts have been used as main coagulants.

Table 2.9: Comparisons of various coagulant aids in water and wastewater treatment

Chemical class	Chemical	Advantages	Disadvantages	References
Synthetic cationic polymers	Polydiallyldimethyl ammonium chloride (poly-DADMAC) -Polydimethyl aminomethyl polyacrylamide -Polyvinylbenzyl -Trimethyl ammonium chloride	-Produces denser shear-resistant sludge. -For the use with metallic coagulants.	-Increases complexity of coagulation-flocculation stage but improves process performance and economy when used properly.	R&D, 2010; Bratby, 2006; Nozaic, et al., 2001; Schulz and Okun, 1984
Synthetic neutral polymers	-Polyacrylamides -Polyethylene oxide			
Synthetic anionic polymers	-Hydrolyzed polyacrylamides -Polystyrene sulfonate -Polyacrylic acid -Polyacrylates	-Produce larger shear resistant flocs by promoting bridging.		

Table 2.9: Continued

Chemical class	Chemical	Advantages	Disadvantages	References
Adsorbent weighting agents	-Calcium carbonate -Bentonitic clays -Fuller's earth clay -Other adsorptive clays	-Cheaper additives for increasing settling velocity, reducing dosage. -Assist in coagulation of waters containing high colour or low turbidity by providing additional suspended matter to the water upon which flocs can form. -Dosages in the range of 10 to 50 mg/L may result in good floc formation, improved removal of colour and organic matter and a broadening of the pH range for effective coagulation. -Ease of storage, handling and application for treatment purposes. <u>Remarks:</u> -In low turbidity waters less than 10 NTU, addition of adsorptive clays may reduce the dosage of alum required. -Calcium carbonate approximately 20 mg/L can also be added to supply alkalinity.	-Increases complexity of coagulation-flocculation, but improves process performance and economy when used properly.	Luu, 200; Schulz and Okun, 1984

2.11 Plant-Origin Coagulants

According to Sciban et al. (2009), natural coagulants extracted from microorganisms and animal or plant tissues are workable alternatives to synthetic polyelectrolyte because they are biodegradable and are presumed to be safe for human health. Therefore, replacing these chemical coagulants with natural coagulants is preferable to counteract the aforementioned drawbacks, and using natural coagulants is valuable in improving the coagulation process.

In this sense, natural coagulants are becoming a central focus of numerous researchers because of their abundant source, low cost, multiple functions, biodegradable qualities (Zhang et al., 2006), and wider effective dosage range of flocculation for various colloidal suspensions (Sanghi et al., 2006). Natural coagulants are also often available locally, thus offering an economically viable choice that is non-polluting (Sanghi et al., 2002).

The use of natural coagulants produces a smaller volume of clarification sludge than the use of metallic coagulants (Ndabigengesere et al., 1995). This characteristic has been proven by the findings of Narasiah et al. (2002), who state that natural coagulants produce readily biodegradable and less voluminous sludge that amounts to only 20%–30% of its alum-treated counterpart. Moreover, sludge produced from clarification processes that use natural coagulants does not contain added metals or toxic compounds.

Natural coagulants have been used to treat drinking water for many centuries (Yin, 2010; Sanghi et al., 2002). For example, Sanskrit literature from India reported the use of seeds from the Nirmali tree (*Strychnos potatorum*) to clarify turbidity in

surface water over 4000 years ago (Schultz and Okun, 1984). In the 16th and 17th centuries, militaries of Peru used roasted and ground corn beans (*Zea mays*) for this purpose. However, these materials have not been widely used because of the lack of scientific understanding of their mechanism and effectiveness. Recently, interest was renewed in the use of natural coagulants of plant origin. Thus, to provide a focused discussion, natural coagulants derived from non-plant sources, such as chitosan (a product typically derived from the waste of shellfish), are excluded from this review because it is beyond the current scope of the research.

The use of these natural coagulants represents an environmentally friendly aspect, and their benefits somewhat offset their disadvantages. The material that has received the greatest degree of attention is the seed of *M. oleifera.* The *M. oleifera* tree, commonly known as drumstick and horseradish, is a native of Northern India and is widely grown throughout the tropics. The tree is drought resistant, fast growing, and grows even in poor soils. Moringa is a tropical plant that belongs to the family *Moringacea*.

Many researchers have reported on the various uses of *M. oleifera* and as a coagulant, especially in the last 23 years (Bhatia et al., 2007; Kebreab et al., 2005; Birima et al., 2003; Muyibi & Alfugara 2003; Muyibi et al., 2003, 2002, 2001; Diaz et al., 1999; McConnachie et al., 1999; Muyibi and Evison 1999; Okuda et al., 1999; Ndabigengesere and Narasiah, 1998; Ndabigengesere et al., 1995; Muyibi and Evison 1996, 1995; Muyibi and Okuofu, 1995; Gassenschmidt et al., 1995; Jahn, 1988, 1984). These studies have found that the *M. oleifera* seed is nontoxic and is a good coagulant in water treatment.

Encouraged by the results of the studies, many developing countries have turned to using this plant as a viable coagulant in water and wastewater treatment on a small scale (Ndabigengesere et al., 1995). Soluble extracts of *M. oleifera* seeds have been studied as a natural coagulant, and the active ingredient has been suggested to be positively charged water-soluble proteins (Bhatia et al., 2007; Ndabigengesere et al., 1995). These proteins bind to the suspended particles, forming large agglomerated solids. Other laboratory studies have so far shown that *M. oleifera* seeds possess effective coagulation properties (Muyibi and Evison, 1995) and are not toxic to humans or animals. The seeds are quite efficient in reducing turbidity and microorganisms from raw waters.

Studies also indicated that the cactus has similar properties with those of the *M. oleifera* seeds; hence, it also has a potential as a coagulant. Cactus mainly originates from the torrid regions and the subtropics. It has recently received a great deal of attention because of its nutritious and medicinal components, such as proteins, amylose, malic acid, resin, vitamin, and cellulose.

Zhang et al. (2006) studied the coagulation performance of *C. opuntia* to act as a natural macromolecular coagulant and discovered high efficiencies in turbidity removal. From the experiments, the optimum dosage for *C. opuntia* to reach 94% turbidity removal was about 50 mg/L. Diaz et al. (1999) used synthetic water with added kaolin to create turbidity in order to study *Cactus latifera* and the seeds of *Prosopis juliflora* as natural coagulants. These two plants are indigenous to Venezuela and have similar properties to those described for natural coagulants. Using jar test measurements, both materials produced comparable turbidity removals,

from an average of 5 NTU to 150 NTU. The findings were similar to those obtained for *M. oleifera* extracts, and compared to the aluminum sulfate dose, the two plant sources required lower doses.

Thus far, the identification of the use of natural coagulants for wastewater treatment has been limited to academic research. Many findings from these academic studies, however, indicate the promising potential of natural coagulants for wastewater treatment. Early studies suggested that plant–origin coagulants can be effectively used to treat selected dyeing effluent. Mishra and Bajpai (2006) conducted an experiment using *Tamarindius indica* mucilage for colour removal, that is, to remove vat and direct dye from aqueous solutions. Approximately 60% of the vat dye was removed in their study, leading them to conclude that *T. indica* is a simple and efficient treatment from an economic and technical perspective. In other literature, Beltràn-Heredia et al. (2009) found that up to 80% Alizarin Violet 3R dye removal can be easily achieved by using tannin-based coagulants.

Furthermore, the applicability of natural coagulants extracted from seeds of plants indigenous and abundantly available in Europe, including *Aesculus hippocastanum* (horse nut) from family *Sapindaceae*, *Quercus robur* (common oak), *Quercus cerris* (turkey oak), *Quercus rubra* (Northern red oak), and *Castanea sativa* (European chestnut) from family *Fagaceae,* was investigated for their possible use in a decentralized water treatment system (Ŝćiban et al., 2009). Among them, extracts from the seeds of European chestnut and common oak acorn were the most efficient coagulants, expressing the highest coagulation activities of around 80% for the chestnut and 70% for the common oak in both low and medium water turbidities.

Dragon fruit (Idris et al., 2013), banana stem juice (Alwi et al., 2013), *C. alata* (Aweng et al., 2012), *Hibiscus rosa sinensis* (Awang et al., 2012), and *Psyllium* husk (Al-Hamadani et al., 2011) are among the uncommon plant-origin active coagulant extracts, aside from the aforementioned established plant coagulants. The potential of these materials as natural coagulants in wastewater treatment has been tested individually or in conjunction with a synthetic coagulant.

Based on this fact, the present study is oriented toward the possible use of *D. esculentum* (pucuk paku) leaves as coagulant and coagulant aid to treat landfill leachate via coagulation–flocculation. However, the use of *D. esculentum* leaves as potential coagulant for landfill leachate treatment has never been investigated in extant literature. The potential transformation of *D. esculentum* from plant to natural coagulant must be explored to assess its removal performance.

2.12 *Diplazium esculentum* (pucuk paku)

Fern is among the 12,000 species of plants that belong to the botanical group *Pteridophyta*. Similar to other vascular plants, ferns have stems, leaves, and roots. They reproduce via spores and do not produce seeds or flowers. *D. esculentum* is classified under *Polypodiopsida,* which belongs to the *Athyriaceae*/*Woodsiacea* family. *D. esculentum* pertains to the edible, young leaves of a fern. Locally known as pucuk paku in Malaysia, these plants are widespread throughout India, China, Cambodia, Laos, Thailand, and Vietnam. They are usually found near river and swamp areas. Figure 2.13 shows an image of *D. esculentum.*

The terrestrial fern grows up to 1 m with a 35 cm stalk and erect, scaly rhizomes. The leaves are bipinnate, the leaflets vary in size, the margin is crenate or lobed, and the sori lines are spread throughout the veins (Amit and Singh, 2012). Table 2.10 shows a nutritional analysis of *D. esculentum*.

Table 2.10: Nutritional value of *Diplazium esculentum*

Moisture	% on dry matter basis				mg/100g		
%	Ash	Fat	Protein	Carbohydrate	Na	K	Ca
93.1	18.8	29.0	37.7	14.5	8.1	927.4	200.5

(Source: Ministry of Environment and Forests, Government of India, 2013)

Figure 2.13: *Diplazium esculentum*

Ferns have been used by human beings as traditional medicine for a long time. Native tribes in India believe that ferns can counteract constipation (Kala, 2005) and can be consumed as an appetizer (Das et al., 2013). The decoction can cure hemoptysis and coughs, while the rhizomes can be used as insecticides (Das et

al., 2013; Kaushik et al., 2011; Kaushik et al., 2003). According to the Human Metabolome Database (2013), *D. esculentum* comprises esculentic or Asiatic acid, which contains lipids with free hydroxyl (–OH) surface groups (Figure 2.14).

Tripathi et al. (1976) and Sen and Bulusu (1962) found that Nirmali seed extracts, which are used as anionic coagulants in water treatment, also comprise lipid, carbohydrates, and free –OH groups. Therefore, *D. esculentum* leaves have the potential and capability to enhance the coagulation process because they also contain similar coagulating active agent such as lipid and free hydroxyl (-OH) as that of Nirmali seed extracts. Given that *D. esculentum* originates from tropical areas, this new natural coagulant must be explored by using local, cheap, and widely available resources in Malaysia. Other coagulation-active components that can contribute to the properties of *D. esculentum* as a coagulant and coagulant aid may also be found in the leaves of this fern.

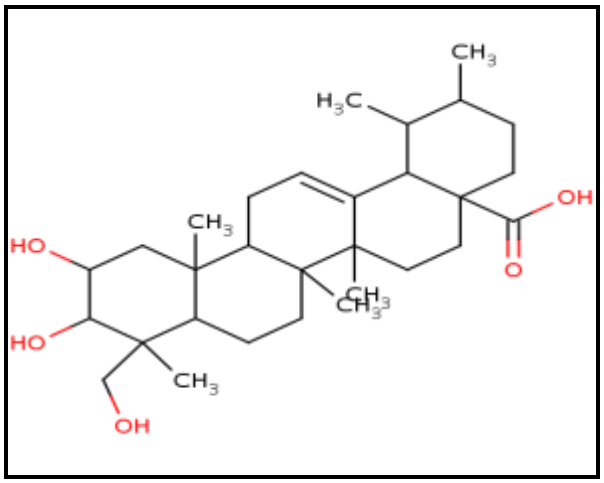

Figure 2.14: Esculentic acid structure in *Diplazium esculentum* (Source: Human Metabolome, 2013)

Elemental analysis (Table 2.11) was performed to provide a preliminary comparison between the elemental compositions of the *D. esculentum* leaves with those of the established plant-based coagulant *M. oleifera*. This type of analyses is especially useful for organic compounds as well as to help ascertain the structure and purity of a synthesized compound (Fadeeva et al., 2008). Generally organic compounds contain primarily carbon, hydrogen and nitrogen.

The *D. esculentum* leaves contained 30.88% nitrogen (N), 4.40% carbon (C), and 1.31% hydrogen (H). As shown in Table 5.3, the carbon percentage of the shelled and non-shelled *Moringa* was higher than that of *D. esculentum* leaves. This finding could be attributed to the composition of *Moringa*, which comprises more organic matters compared to *D. esculentum* leaves.

Table 2.11: Elemental analysis of natural coagulants

Parameters	Shelled *Moringa* seeds[a]	Non-shelled *Moringa* seeds[a]	*D. esculentum* leaves (This study)
N (%)	6.1	5.0	30.88
C (%)	54.8	53.3	4.40
H (%)	8.5	7.7	1.31

(Source: [a] Ndabingengesere et al., 1995)

2.13 Extraction Methods for Plant Origin Coagulants

Active components are generally extracted from the seeds, bark or sap, roots, and fruits of trees and plants (Pritchard et al., 2009). Researchers tend to extract natural coagulants in powder form for further use when dealing with the synthesis of natural coagulants. However, the powder form is usually rich in organic components, which may exacerbate the treated sample.

To improve treatment efficiency, active components may be extracted by using different solvents, such as organic materials (i.e., petroleum ether, acetone, chloroform, and hexane), water, or salt solution (i.e., KCl, NaCl, $CaCl_2$, and NH_4Cl). Although the use of leaf extracts as coagulants has never been investigated in previous literature, a limited number of studies have used leaves as adsorbents to remove heavy metals and methylene blue in solutions. These studies involve the use of *Hevea brasiliensis* (rubber) (Ngah and Hanafiah, 2008), *Imperata cylindrica* (lalang) (Hanafiah et al., 2007), and grass waste (Hameed, 2009) without the addition of chemicals. This study follows the proposed method of Awang and Aziz (2012) (Section 4.3).

Aside from using *D. esculentum* without chemical or physical treatment, the powdered leaves of *D. esculentum* are treated with thioglycolic acid as previously described by Okieman et al. (1987) and Horsfall and Aiba (2003) to explore whether chemical treatment contributes to the coagulation activity (CA) of *D. esculentum*. Table 2.12 lists several options to investigate the coagulation extraction techniques of various plant origins.

Table 2.12: Several techniques for various plant origin coagulant extractions in literature

References	Natural Coagulant	Wastewater	Extraction process	Findings
Alwi et al., 2013	Banana stem juice	Coolant	The thorns were removed and the pith of the stem was then separated from the foliage. 100 g of small pieces of the pith were mix with 10 mL of distilled water using a mixer. The mixed pith was the filtered and the juice was collected. The fresh juice of banana stem was stored in a refrigerator at 7 °C to ensure its freshness. The coagulation experiments using banana stem juice were carried out on the same day to avoid any fermentation process.	At pH 7 and 90 mL dosage ,the highest recorded COD, SS and turbidity removal percentages were 80.1%, 88.6& and 98.5% respectively.
Idris et al., 2013	Dragon fruit foliage	Latex effluent	Thorns of dragon fruit were removed and the foliage was subsequently washed, cut and dried at 80 °C. It was blended into fine powder and sieved to a particle size range of 0.45 – 1.25 mm.	At pH 10, the percentage removal of COD, SS and turbidity were 94.7 %, 88.9 % and 99.7 % respectively.
Aweng et al., 2012	*Cassia alata* (pokok gelenggang)	Raw surface water	The leaves were dried in oven for two days at 50 °C. The dried leaves were then ground with a laboratory grinder. All grinded materials were passed through 0.4mm sieve and the sieved materials were used for extraction process. Crude extract was prepared using 1L of distilled water to 50g of the prepared powder, mixed by a magnetic stirrer for 60min and left to settle for 20 min. The crude extract of *Cassia alata* was finally filtered through 0.95mm filter paper.	Removal turbidity up to 93.33% at the optimal dosage of 1.0mL/L.

Table 2.12: Continued

References	Natural Coagulant	Wastewater	Extraction Process	Findings
Šćiban et al., 2009	-Chestnut (*Aesculus hyppocastanum* and *Castanea sative*) -Acorn (*Quercus robur*, *Quercus cerris* and *Quercus rubra*)	Synthetic turbid water	The seeds were ground to fine powder using laboratory mil (separately for each chestnut and acorn). All grounded materials were sieved through 0.4mm sieve and the fraction with particle size less than 0.4 mm was used. 50g of prepared powder was suspended in 1 L of distilled water or NaCl solution and the suspension was stirred using a magnetic stirrer for 10 min to extract the coagulation active components. The suspension was then filtered and kept in refrigerator for further used.	Coagulation capabilities to remove turbidities from synthetic water depend on pH. Highest coagulation activity derived from *Ae.Hyppocastanum* and *Q. robur* were 70% and 80%, respectively, at low dose, 0.5 ml/L.
Anastasakis et al., 2009	-Mallow (*Malva sylvestris*) -Okra (*Hibiscus esculentus*)	Biologically treated effluent	The seedpods of the plant were initially washed thoroughly with water to remove any impurities, dried at 110 °C for 6 h and then ground with a microhammer cutter mill and sieved to a 32 mesh (500μm) particle size.	With the help of 0.025 Mm Al^{3+} addition(no pH controls), 62.5 mg/L mallow and 2.5 mg/L okra successfully removes 63% and 72% turbidity respectively,
Mishra and Bajpai, 2006	*Tamarindus indica*	Textile effluents	Seeds were thoroughly washed and soaked in distilled water overnight. The mucilaginous extract was filtered through muslin cloth. It was precipitated by adding three parts of iso-propanol to one part of the aqueous extract. The residue was then washed with acetone two or three times to remove impurities and finally dried by keeping it in an oven at 40 °C for 24 h.	At neutral pH, the maximum removal was 60% for golden yellow after 2 h and 25% for direct fast scarlet after 1 h. The optimum mucilage dose was 10 mg/L and 15 mg/L respectively.

2.14 Mechanisms in coagulation process

Destabilization mechanisms for metal coagulants in the coagulation process include electric double-layer compression, adsorption, interparticle bridging, and precipitation enmeshment (or sweep flocculation) (Wei et al., 2009; Dominguez et al., 2007; Bratby, 2006; Duan and Gregory, 2003) On the other hand, bridging and electrostatic patch effects are considered the primarily destabilization mechanisms of flocculation with polymers (Bache and Gregory, 2007; Bratby, 2006).

2.14.1 Metal Coagulants

Electrical double layer compression occurs due to the increase of ionic strength by coagulation addition. If this layer is sufficiently compressed, the van der Waals force predominates across the entire area of influence to enhance the attractiveness of the net force and eliminate energy barriers. Therefore, as the forces of repulsion are suppressed, the gentle mixing results in the particle contact and the forces of attraction that stick particles to one other generate a progressive agglomeration, as shown in Figure 2.15 (Hammer and Mark, 2004).

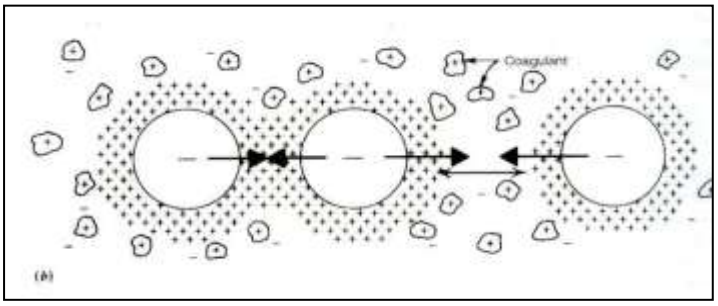

Figure 2.15: Compression of the double layer charge on colloids (Source: Hammer and Mark, 2004)

Adsorption occurs when negatively charged particles adsorb onto positively charged metallic complexes and neutralize the charge to bind themselves together. When the surface charge is neutralized, the particle interactions are dominated by the van der Waals forces, allowing for rapid coagulation. Charge reversal can take place with increasing dose and continued adsorption to increase the energy barrier and restabilize the suspension (Bache and Gregory, 2007).

In terms of bridging mechanism, large molecules may be formed when aluminum or ferric salts are dissociated in water. Synthetic polymers may also be used instead of or in addition to metallic salts. These highly surface-reactive polymers may be either linear or branched. Therefore, several colloids may be attached to one polymer and several polymer colloid groups may be enmeshed to produce a settleable mass (Peavy et al., 1985).

Precipitation enmeshment involves the addition of relatively large doses of coagulants. Aluminum or ferric salts are usually precipitated as hydrous metal oxides. The significance of precipitation enmeshment increases along with the increasing dose of coagulants. The amount of used coagulants exceeds the required amount for neutralizing the charge on the colloid, hence increasing the concentration of enmeshing the solid surface area. Some charges may be neutralized in this process, but most of the colloids are literally swept from the bulk of the water by becoming enmeshed in the settling hydrous oxide floc. This mechanism is often called sweep flocculation. Figure 2.16 shows a schematic of the events that may possibly occur during the interaction of the aluminum species with the negatively charged particles in the water.

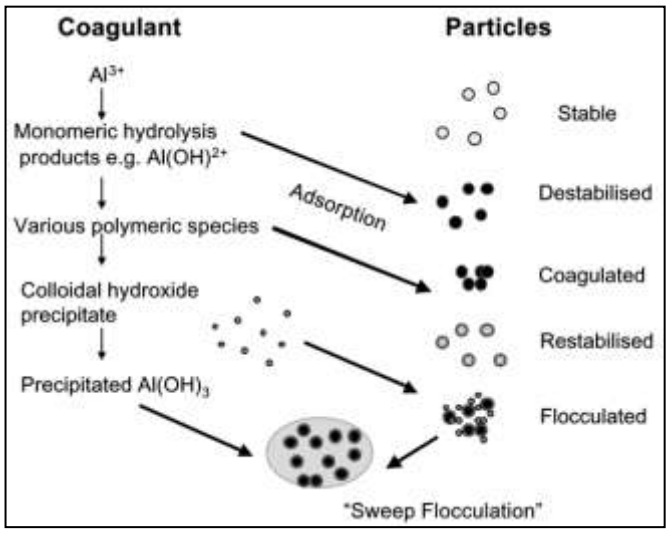

Figure 2.16: The interaction of aluminum species with initially negatively charged particles in water (Source: Duan and Gregory, 2003)

2.14.2 Polymer as Primary Coagulant

As expounded in the preceding section, the polymer molecules become either positively or negatively charged depending on the functional groups present (Bratby, 2006; Bolto and Gregory, 2007). According to the experimental data (Section 4.3), it can be concluded that both DEaqs and DEpowd were anionic polymers. However, this study will elucidate more on bridging since it is the main mechanism involved in DEaqs and Depowd.

2.14.2.1 Bridging

Anionic polyelectrolytes can be absorbed on negatively charged surfaces despite electrostatic repulsion in many cases. But, this only occurs if there is a sufficient concentration of divalent metal ions (Berg et al., 1993). It is very likely that ions such as Ca^{2+} can represent as ‘bridges, between anionic groups on the polymers and the negative sites on the surfaces. Some negatively charged particles can be readily flocculated by anionic polyelectrolytes at fairly low calcium concentrations (around 1 mM or more). However, in the absence of divalent cations, no flocculation occurs; even at quite high ionic strengths.

This is in line with Henderson and Wheatly (1987) where flocculation by anionic polyacrylamide (PAM) was adversely affected by the presence of multivalent ions such as Fe^{3+} . This was due to complexation of the metal with carboxylate groups on the polymer chain and thus an effective reduction in charge density (CD). Hence, as aforementioned above, the adsorption of anionic polyelectrolytes on negative surfaces require a certain concentration of divalent metal ions.

Although polymer adsorption is essentially irreversible in many cases, there are examples where desorption of polymer chain can occur. For example, with a range of molecular weight (MW), small molecules may adsorb first (because of their faster diffusion) and then be gradually displaced by higher MW material (Bolto and Gregory, 2007; Lipatov et al., 2005). Long chain polymers adsorb on particles in the maner of ‘dangling ‘segments as depicted in Figure 2.17. Polymers can have loops and tails extending some way into solution thus bridging particles together (Figure 2.18a) (Bolto and Gregory, 2007). The polymer dosage should be sufficient to attach

on particle's surface, otherwise the particle's surface will become saturated leading to restabilization (Figure 2.18b) (Aziz et al., 2007).

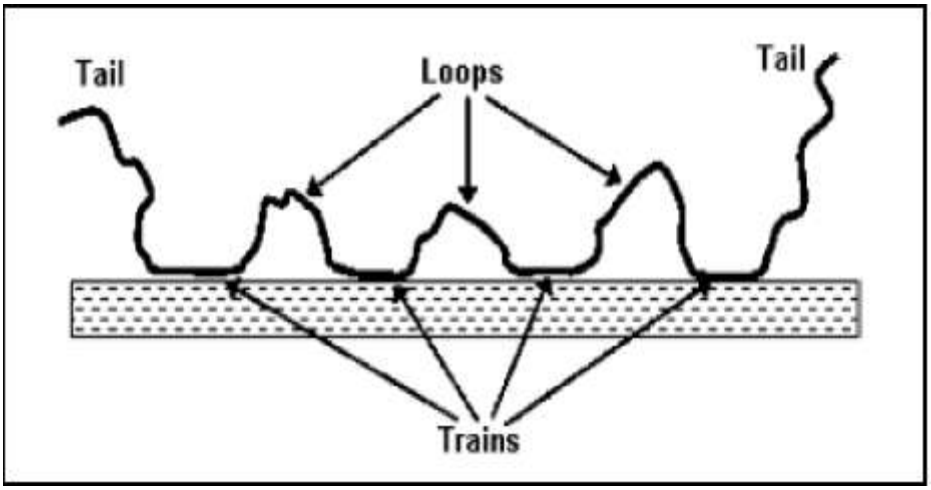

Figure 2.17: Model of an adsorbed polymer chain (Source: Bolto and Gregory, 2007)

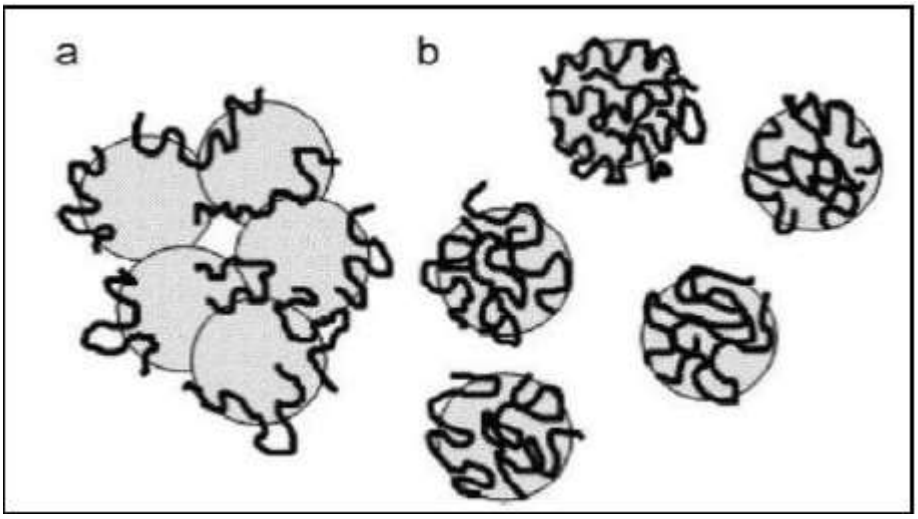

Figure 2.18: Schematic picture of (a) bridging flocculation and (b) restabilization by adsorbed polymer chains (Source: Bolto and Gregory, 2007)

2.14.3 Polymer as Coagulant Aid

Organic polymer can also be applied as coagulant aid to bridge the coagulated particles formed when metal salts have been used as the primary coagulant (Bolto and Gregory, 2007). An appropriate polyelectrolyte can increase floc size;a strong dense floc of regular shape is preferred. Bolto and Gregory (2007) explained that an electrostatic patch occurs when highly charged cationic polymer adsorbs on a weakly charged negative surface to give overall neutrality, each surface-charged site becomes physically impossible to neutralize by a cationic polymer because the average distance between the surface site is greater than that between the charge carried by the cationic coagulant. As shown in Figure 2.19, although the surface may have a near-neutral overall charge, patches or islands of positive charge appear between the regions of the uncoated, negatively charged surface.

Consequently, an electrostatic attraction occurs between positive patches and negative areas as the particles approach one another, leading to particle attachment and inducing flocculation. The positive patches on the particle surface may also serve as an anchor point for the adsorption of anionic polyelectrolytes with high molecular weight. This effect is called the dual coagulant system (Figure 2.20). Given the limited number of positive patches, an anionic polymer chain cannot form multiple attachments on the surface, but will tend to adopt an extended configuration from the surface to allow for greater bridging opportunity (Bolto and Gregory, 2007; Bolto, 1995).

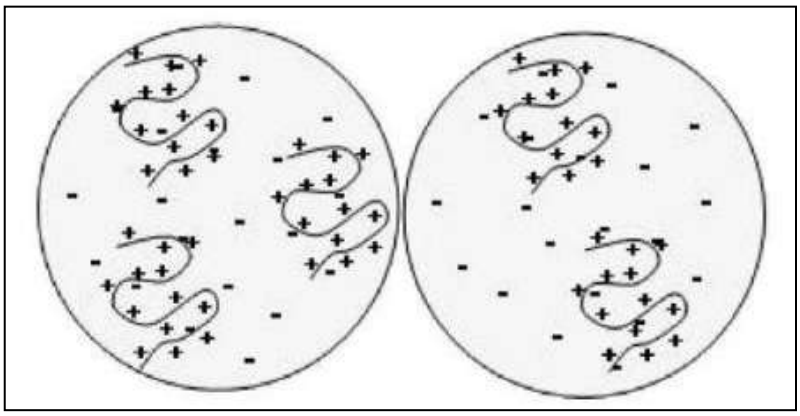

Figure 2.19: Electrostatic patch model for flocculation of negative particles by cationic polyelectrolytes (Source: Bolto and Gregory, 2007)

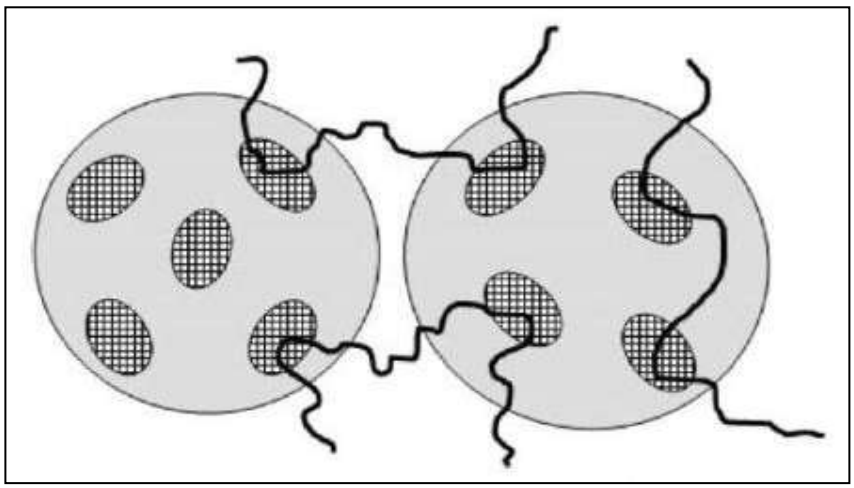

Figure 2.20: Possible mode of adsorption and flocculation by anionic polymers on particles with cationic patches (Source: Bolto and Gregory, 2007)

2.15 Factors Affecting the Coagulation Process

The coagulation process can be affected by several factors, such as primary coagulant dosage, mixing effects, pH/alkalinity, temperature, and colloid concentrations. These factors, individually and collectively, have a great influence in determining the effectiveness of coagulation processes.

The maximum settling and removal of suspended particles can be efficiently and effectively achieved by using an optimum dose of coagulants. This dosage is defined as the value in which a further addition of coagulant does not significantly enhance the removal efficiency (RE) (Aguilar et al., 2005). A low dosage cannot adequately destabilize particles. The limit of acceptable dosages varies with every coagulant, with some coagulants showing less sensitivity to imprecisely measured dosages. This limitation has led to the definition of the four zones of coagulant dosage (Duan & Gregory, 2003) with the following consequences:

Zone 1: Low dosage, particle still negative and stable

Zone 2: Sufficient dosage giving charge neutralization

Zone 3: Higher dosage giving charge neutralization and restabilization

Zone 4: Highest dosage giving hydroxide precipitation and sweep flocculation

Similarly, the removal of particulate matter can be effectively aided by an optimum range of mixing times. The coagulation process mainly involves three phases of mixing: rapid mixing, slow mixing, and no mixing. Rapid mixing is a short period of extremely turbulent mixing that allows coagulants to make contact with

suspended particles. This phase is followed by flocculation, which involves slow mixing to allow the agglomeration of destabilized particles into larger particles. No mixing allows the flocculated particles to settle out of the system. An insufficient time for slow mixing results in the poor agglomeration of particles, whereas a prolonged agitation leads to the rupturing of the floc fragment and the disagglomeration of particles (Culp et al., 1974).

Coagulation is also affected by water-based variables such as pH and alkalinity (Hudson, 1982). Alkalinity refers to the buffering capacity of the water and its capability to neutralize its acid contaminants. Alkalinity and pH are generally related; waters with high alkalinity have high pH. The acidic characteristic of the metal coagulant reduces alkalinity during the addition of a coagulant. If the wastewater has low alkalinity, the addition of a coagulant may consume all the available alkalinity and reduce the pH value. This condition does not present a favorable situation for the coagulation process. Coagulants such as alum and ferric chloride are more acidic than PACl. Therefore, the addition of these coagulants may result in greater alkalinity consumption. For PACl, alkalinity consumption is related to basicity. A PACl with high basicity consumes lesser alkalinity. The pH must be controlled because the coagulation occurs within a specific range for each coagulant (Bratby, 2006; Aguilar et al., 2005).

The solubility of a coagulant is strongly affected by pH. For example, $Al(OH)_3$ is amphoteric in nature and soluble at low and high pH, and the adsorption mostly occurs in the pH range with minimum solubility. Alum demonstrates a favorable coagulating performance in the pH region near 5 and 7. Under these

conditions, the positively charged aluminum hydroxide neutralizes the negatively charged particles, which results in zero zeta potential. However, the coagulant restabilizes at pH ranging from 5 to 7 because of the charge reversal caused by the excessive adsorption of positively charged aluminum hydroxide species. Table 2.13 shows the optimum pH ranges for some metallic salts.

Table 2.13: Optimum pH values for metallic coagulants

Coagulants	pH
Aluminum sulphate	4.0 to 7.0
Ferrous sulphate	8.5 and above
Ferric chloride	3.5 to 6.5 and above 8.5
Ferric sulphate	3.5 to 7.0 and above 9.0

(Source: Alley, 2007; Shammas, 2005)

Metal coagulants perform poorly at low temperature because such temperature level affects the coagulation process by altering the coagulant solubility, increasing the water viscosity, and retarding the kinetics of hydrolysis reactions and particle flocculation.

High coagulant dose, the addition of flocculation or coagulant aids, and longer flocculation time are often required to produce treated water with low turbidity. Polyaluminum coagulants are considered more effective than alum in cold water because such coagulants are pre-hydrolyzed. The superiority of PACl over alum under cold-water conditions has been widely reported (Dempsey et al., 1994; Edzwald et al., 1994).

Colloid concentration has a major effect on the coagulation process and the coagulant demand. The amount of coagulant for the coagulation process is directly related to the amount of colloids present in the water or wastewater. The dilute

colloids in water or wastewater have very slow coagulation rate. Such coagulation rate can be improved by using coagulation aids or recycling settle sludge (Wang et al., 2005).

2.16 Floc

Flocs are highly porous fractal-like aggregates that are composed of many primary particles (Wang et al., 2009). Particle aggregation is an important process that affects the fate of flocs in coagulation and flocculation processes. The properties of aggregated particles, including particle size, shape, and strength, have significant effects on the efficiency of solid/liquid separation processes, such as sedimentation, flotation, and filtration (Li et al., 2007; O'Melia, 1998).

Flocs must resist stress or shear to prevent being broken into small particles and thus improve their characteristics (Wei et al., 2009; Li et al., 2007; Jarvis et al., 2005). The efficiency and cost of water treatment via coagulation are directly influenced by the growth rate, size, strength, and recoverability of flocs (Zhao et al., 2013).

Floc strength is regarded as an important parameter in the coagulation process. It depends on the structure, formation mechanisms, and interparticle bonds of flocs (Liu et al., 2009). Flocs with high strength can resist ruptures when they are exposed to shear force. Floc strength can be measured by applying an increasing shear rate to preform flocs. Broken flocs are capable of re-aggregation, which may

improve the subsequent solid/liquid separation efficiency (Yukselen and Gregory, 2004).

Floc formation and breakage by using metal salts and inorganic polymers as coagulants have been investigated in several studies (Wei et al., 2010; Wang et al., 2009; Xu et al., 2009; Jarvis et al., 2006; Yukselen and Gregory, 2004). These studies found that stirring conditions significantly influence floc growth. Although they may grow to a limited size in some cases, flocs may also fluctuate in size under the same agitation conditions (Jarvis et al., 2004; Gregory and Rossi, 2001).

2.17 Coagulation in Landfill Leachate Treatment

Bound by research scope, only landfill leachate coagulation-flocculation using PACI and plant-origin coagulants were reviewed in this particular section. Optimum dosage and pH for PACI application in each study were distinctive due to its leachate characteristics.

Summary of literatures regarding PACI application in landfill leachate studies is shown in Table 2.14. Studies regarding combinations of PACI coagulation with other treatment methods have been excluded since it is beyond current research scope. Meanwhile, Table 2.15 summarizes the application of plant-origin coagulants for landfill leachate treatment. However, the performance of plant-origin coagulants for landfill leachate treatment seems restrained and not well documented.

Table 2.14: Literature on PACI application in landfill leachate coagulation-flocculation treatment

Coagulant	Landfill	Landfill/leachate type	Findings	Remarks	Authors
PAC 18%	Pulau Burung Landfill Site, Pulau Pinang, Malaysia	Semi-aerobic operating landfill	-Removal of colour (91%), COD (55%) and colour (80%). -Optimum dosage: 7200 mg/L	-PAC efficiency was comparable to alum, but PAC required less dosage. Combination of optimum dosage and optimum pH was not considered in the study.	Al-Hamadani et al., 2011
			-Removal of colour (83%), COD (56%) and colour (91%). -Optimum pH: 7.5		
			-Removal of colour (97.26%), COD (56.76%), colour (99.22%) and turbidity (99.18%). -Optimum dosage: 1900 mg/L -Optimum pH:7.5	-Although PAC was less effective than alum in COD removal, the dosage used was just 1/5 that of alum.	Ghafari et al., 2010

Table 2.14: Continued

Coagulant	Landfill	Landfill/leachate type	Findings	Remarks	Authors
PAC 18%	Pulau Burung Landfill Site, Pulau Pinang, Malaysia	Semi-aerobic operating landfill	-Removal of colour (90.7%), COD (43.1%), SS (99.22%) and turbidity (99.18%). -Optimum dosage: 1900 mg/L -pH: 7.5	-Coagulation was optimized using response surface methodology (RSM).	Ghafari et al., 2009
			-Removal of colour (97%), COD (61%), SS (99%) and turbidity (99%). -Optimum dosage: 1900 mg/L -pH: 7.5	Most efficient rapid/slow mixing speed and time were determined as follows: Rapid mixing: 80 rpm, 45 s; Slow mixing: 40 rpm, 15 min; and settling time: 30 min.	Ghafari et al., 2005
PAC	Shuangkou Town Sanitary Landfill, Tianjin, China	Sanitary landfill	-Removal of COD (61%), SS (93%) and turbidity (99%). -Optimum dosage: 0.5-0.6 g $Al^{3+;}$ -Optimum pH: 5.5	-Sludge generated by PAC was greater than that of alum and ferric chloride. PAC>$Al_2(SO_4)_3$>$FeCl_3$>PFS.	Li et al., 2010

Table 2.14: Continued

Coagulant	Landfill	Landfill/leachate type	Findings	Remarks	Authors
Aluminium polychloride (PAX) 18%	La Zoreda Asturias Sanitary Landfill, Spain (Central landfill)	Operating landfill (24 years old); Mixture of old and young leachates (due to new landfill.	Old leachate: -Removal of colour (96.8%), COD (61.6%) and turbidity (97.9%). -Optimum dosage: 4000 mg/L -pH: 8.3 (initial leachate pH)	-PAC dosage of 1 g/L was selected for economical and environmental reasons since the turbidity removal is similar to that of 4 g/L. Volume of sludge generated was 2-3-fold than that of ferric chloride. Maximum COD removal was generally lower for young leachate (35%) compared to old leachate (73%). Coagulant aids were proposed for better floc settleability.	Castrillón et al., 2010
			Young leachate: -Removal of colour (91.2%), COD (36.8%) and turbidity (97.7%). -Optimum dosage: 4000 mg/L -pH: 8.3 (initial leachate pH)	Results suggested that pH adjustment might not be required for optimum removal. Sludge generation is greater than alum and ferric chloride	Marañón et al., 2008

Table 2.14: Continued

Coagulant	Landfill	Landfill/leachate type	Findings	Remarks	Authors
PAC- 18	Thessaloniki Municipal Landfill,N. Greece	-	-Removal of COD (62%) and SS (98%). -Optimum dosage: 11 mM -pH: 5.5	It performed better decolourisation than ozonation. However, ferric chloride is a better coagulant compared to PAC.	Ntampou et al., 2006
Aluminium polychloride	Merida Municipal Landfill, Yucatan, Mexico	Operating landfill cell (< 4 years old)	-Although no particular numerical results of PAC performance was shown, the comparison between four tested coagulants was stated.	None of the four coagulants tested i.e. ferric chloride, ferric sulphate, aluminium polychloride and aluminium sulphate was adequate for leachate treatment. However, ferric sulphate was the best coagulant.	Méndez-Novelo et al., 2005
Aluminium polychloride	Bordo Poniente Sanitary Landfill, Mexico City	Stabilised saline landfill leachate	-Removal of COD (58%) and SS (96%). -Optimum dosage: 1250 mg/L -pH: 5 – 6	Slightly less effective compared to ferric sulphate, but nearly 50% coagulant dosage could be saved	Monje-Ramírez and Ortade Velásquez, 2004

Table 2.15: Literature on plant origin application in landfill leachate coagulation-flocculation treatment

Coagulant	Landfill	Landfill/leachate type	Findings	Remarks	Authors
Psyllium husk (*Plantago ovata*)	Pulau Burung Landfill Site, Pulau Pinang, Malaysia	Semi-aerobic operating landfill	As primary coagulant: -Removal of COD (17%), SS (41%) and colour (27%). -Optimum dosage : 400 mg/L	Ineffective as primary coagulant due to low zeta potential (-1.92 mV).	Al-Hamadani et al., 2011
			As coagulant aid: -Removal of COD (64%) ,SS (96%) and colour (90%). -Dosage:PAC (7200 mg/L) + Psyllium husk (400 mg/L)	Improvement of coagulation performance is low (≤ 10%); Removal of NH3-N was low; BOD5 removal was lower compared to those of using alum or PAC solely; Optimum pH was not determined.	
			As coagulant aid: -Removal of COD (63%) ,SS (81%) and colour (82%). -Dosage: alum (10000mg/L) + Psyllium husk (400 mg/L)		

Table 2.15: Continued

Coagulant	Landfill	Landfill/leachate type	Findings	Remarks	Authors
Hibiscus leaf mucilage (*Hibiscus rosa-sinensis*)	Pulau Burung Landfill Site, Pulau Pinang, Malaysia	Semi-aerobic operating landfill	As coagulant aid (at pH 10) -Removal of Fe^{3+} (100%) and SS (72%). -Dosage: alum (4000 mg/L)+ Hibiscus leaf mucilage (500 mg/L)	*Hibiscus* leaf mucilage could act as primary coagulant at high pH.	Awang and Aziz, 2012

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter presents the materials and methods which were used in this study. The experimental works to extract *Diplazium esculentum* leaves and jar test were explained thoroughly together with the jar test procedure. Three phases of jar test were performed with PACI, DEaqs and DEpowd on two landfill leachate. In order to evaluate the efficiency of coagulants used, five main parameters were analyzed which were colour, COD, turbidity, NH_3-N and SS. The procedures in each parameter were explained in detailed. The schematic flow diagram showing all the overall experimental activities carried out in this research work is shown in Figure 3.1.

3.2 Landfill Leachate Sampling

3.2.1 Sampling of Landfill Leachate at KSLS

Leachate samples were collected from the KSLS collection pond between October 2010 and November 2012 using a 20 L commercial plastic container (Figure 4.5). A total of 26 samples were collected from the pond. The samples were immediately transferred to the laboratory and stored in a cool room at 4 °C before the experiment to avoid biological activities and changes in the samples.

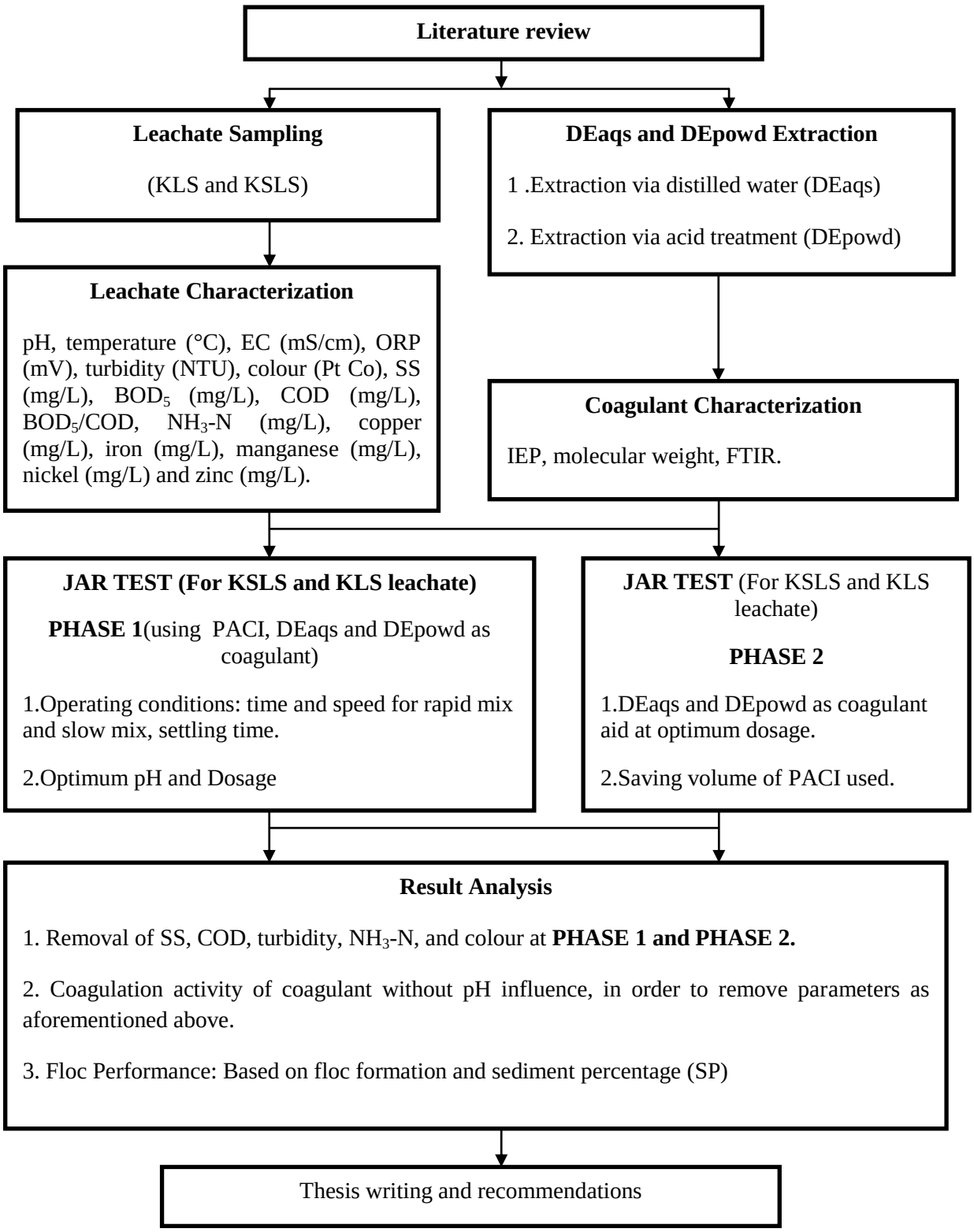

Figure 3.1: Schematic flow diagrams of experimental activities

The samples were collected 30 cm deep from the surface (Figure 3.2). The remaining leachates were collected depending on their retention time in the collection pond. The samples were collected in a mode that represents the entire generated leachate.

Given the landfill design (Abu foul, 2007) and the absence of an aeration process, the generated leachate was considered anaerobic. The collected samples were characterized in terms of pH, temperature (°C), EC (mS/cm), ORP (mV), turbidity (NTU), colour (Pt Co), SS (mg/L), BOD_5 (mg/L), COD (mg/l), BOD_5/COD, NH_3-N (mg/L), copper (mg/L), iron (mg/L), manganese (mg/L), nickel (mg/L), and zinc (mg/L). Before the experiment, the leachate samples were removed from the refrigerator and were placed in about 22 °C for conditioning. The samples were thoroughly agitated for the re-suspension of potential settling solids before any tests were conducted.

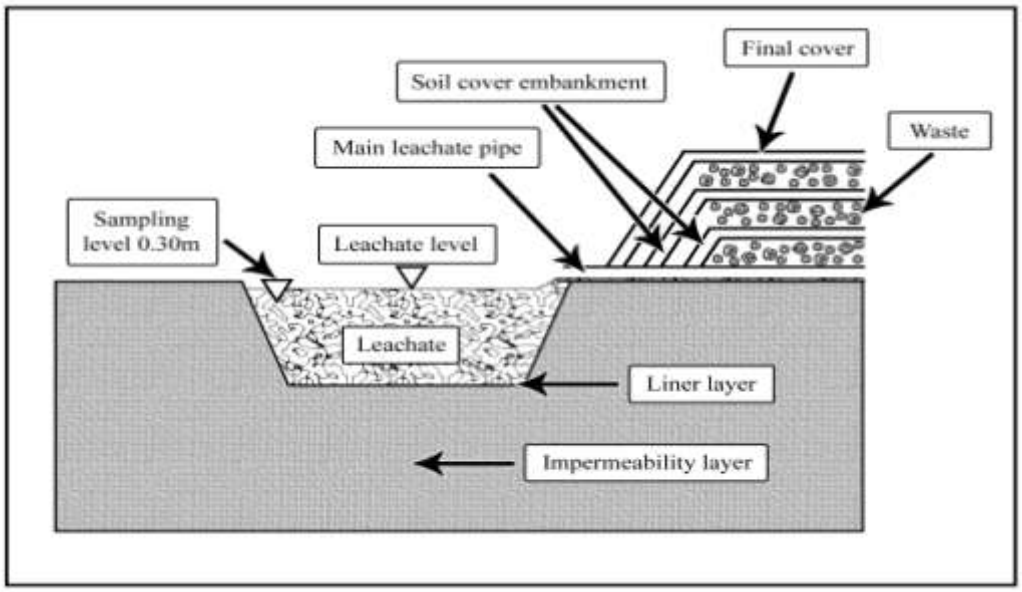

Figure 3.2: Schematic diagram of leachate collection pond at KSLS

3.2.2 Sampling of Landfill Leachate at KLS

Raw landfill leachate samples were collected from the KLS collection pond using 20 L commercial plastic containers (Figure 3.3). A total of 26 samples were collected from October 2010 to November 2012. These samples were transported immediately to the Environmental Engineering laboratory and stored in a dark, cold room at 4 °C to minimize changes in the sample constituents.

The samples were removed from the refrigerator and were left at room temperature before the analyses. The acquisition and storage of leachate samples were made in accordance with the Standard Method for the Examination of Water and Wastewater (APHA, 2005). The samples were collected approximately at 30 cm depth from the surface of the collection pond, which contained raw, untreated leachates. The collected samples representat the 16 parameters mentioned in Section 3.2.1.

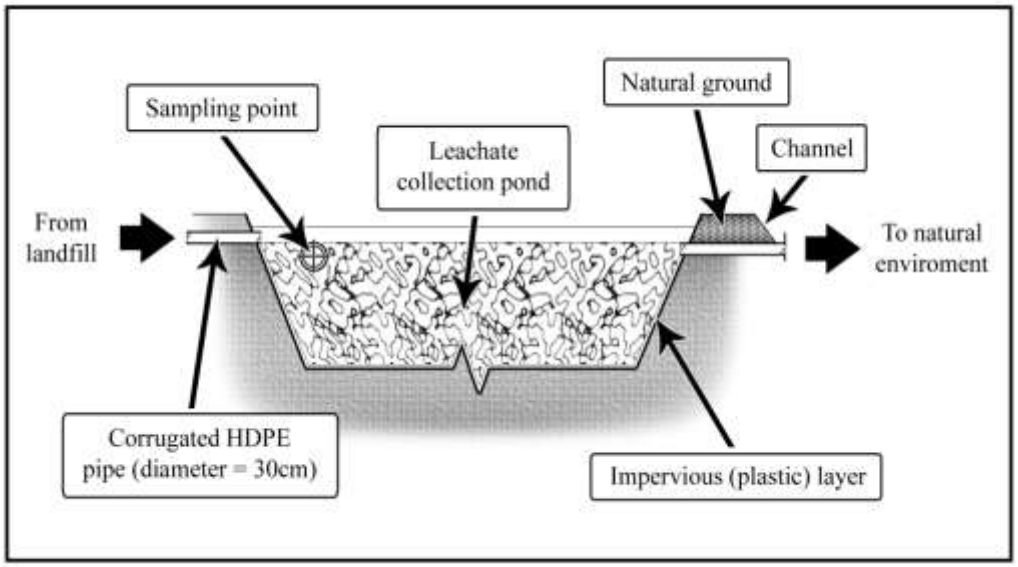

Figure 3.3: Schematic diagram of leachate collection pond at KLS

3.3 *Diplazium esculentum* leaves Extraction Procedures

3.3.1 Extraction via distilled water (DEaqs)

D. esculentum leaves were obtained from the local market in Bagan Serai, Perak, Malaysia. The collected fresh leaves were washed repeatedly with water to remove dust and soluble impurities. X_1 g of the green leaves was placed in a beaker containing Y_1 L of distilled water. The mixture was blended using a domestic blender at high speed to extract the active ingredient of *D. esculentum.* The suspension was then filtered into a beaker using 0.45 µm filter paper. The leaf dregs were dried in an oven for 48 h at 105 °C, and the filtrate stock solutions were stirred using a magnetic stirrer (Model: FAVORIT ST0707V2) for 30 min at room temperature. The dry leaf dregs were weighed and the amount was marked as X_2. The pure concentration (M_1) of the dissolved filtrate stock solution (DEaqs) was calculated as follows:

$$M_1 = (X_1 - X_2) / Y_1 \quad (3.1)$$

The weight of fresh *D.esculentum* leaf (X_1) = 201.1256g
The weight of dry *D.esculentum* leaf (X_2) = 100.5461g
Content of *D.esculentum* leaf extract = 100.5795g

Therefore, a total of 100.5795g of *D.esculentum* leaf extract was dissolved in 1L (Y_1) of distilled water.As a result, the pure concentration concentration (M_1) of DEaqs :

Pure concentration concentration of DEaqs (M_1) = 100.5795 g / 1L

= 100 g/L

The 100 g/L of DEaqs filtered stock solutions were used for the coagulation experiments either immediately or after being stored in a cool room at 4 °C to ensure freshness. Plate 3.1 shows the DEaqs filtered stock solution.

Plate 3.1: *Diplazium esculentum* leaves extract juice

3.3.2 Acid Treatment of *D. esculentum* Powder (DEpowd)

The leaves were extensively washed with distilled water, dried in an oven at 105 °C for 24 h, and ground into fine powder using a 1HP Table Type Pulverizing

Machine (Rong Tsong Precision Technology Co.) The dried leaves were screened through a series of mesh sieves to obtain a fine powder of the desired size.

The powdered *D. esculentum* leaves were treated with thioglycolic acid as previously described by Okieman et al. (1987) and Horsfall and Aiba (2003). The finely powdered leaves were activated by soaking 500 g of the powder in 0.3 M HNO_3 for 24 h and by thoroughly washing the powder with deionized water until a pH of 7 was obtained (without using the buffer). The powder was then air-dried. The activated powder was acid treated with 250 mL excess of 1.0 M thioglycolic acid solution and stirred for 24 h at 30 °C while maintaining a pH of 7. The acid treatment process led to the thiolation of the hydroxyl groups on polymer by the following Equation 3.2 to indulge the coagulation properties.

$$\text{polymer} - OH + HSCH_2CO_2H \rightarrow \text{polymer} - SH + H_3CO_2^- + H^+ \quad (3.2)$$

The acid-treated powder was centrifuged at 200 rpm for 5 min and the supernatants were discarded. The powder was then washed with deionized water and re-suspended in 1.0 M hydroxylamine to remove all O-acetyl groups. The powder was air-dried at cold temperature before being stored for further use (Plate 3.2).

According to Bolto and Gregory (2007), the polymers used in water treatment should be water soluble. Therefore, 100 g of DEpowd was added into a 1L volumetric flask and make up to 1L solution with the addition of distilled water to prepare a 100 g/L Depowd due to unknown molecular weight. DEpowd stock solution was then well mixed by using magnetic stirrer with a stir bar for 15 min to extract the coagulation active component. The coagulants were prepared freshly each time of the experimental work.

Plate 3.2: Dried leaves of *Diplazium esculentum* in powder formed

3.3.3 Basic Equation for Calculation of Coagulant Concentration

As mentioned beforehand, coagulants used in this study were in stock solutions including 18% solution of polyaluminum chloride (PACI). The calculation of the stock solution for the studied coagulants was prepared according to Equation 3.3.

The calculation method for the amount of the coagulants needed is shown in Appendix A.

$$M_1V_1 = M_2 V_2 \quad (3.3)$$

Where

M_1 = Initial sample concentration (mg/L)

V_1 = Initial sample volume (mL)

M_2 = Sample concentration required (mg/L)

V_2 = Sample volume required, (500 mL)

3.4 Characterization of Coagulant

3.4.1 Zeta Potential (Surface Charge), Particle Size and Isoelectric point (IEP)

Surface charge and particle size of the effluent, leachate, DEaqs, and DEpowd (only surface charge) were evaluated by determining the electrophoretic mobility of the suspended particles using the Malvern Zetasizer Nano ZS. The measurements were conducted at 25 °C by using distilled water as the dispersed medium. IEP was determined by titrating a 10 mL coagulant using 0.25 M HCL or 0.25 M NaOH with pH values ranging from 3 to 12 or from 12 to 3 depending on the zeta potential at the start of the titration in order to avoid the crossing of IEP in the beginning (Kumpulainen et al., 2008).

3.4.2 Molecular Weight

The molecular weight of DEaqs and DEpowd were determined using Malvern Zetasizer Nano ZS. Four different sample concentrations were prepared by diluting a high-concentration stock solution of DEaqs and DEpowd using toluene and distilled water as solvents respectively. The prepared sample was filtered before use. Scattering intensity was determined using zero concentration samples (if the solvent was not toluene). The data collection and calculation methods were performed using the molecular weight function of the DTS software for the Zetasizer Nano system,

which compiles the static intensity measurements and generates a standard Debye plot.

3.4.3 Fourier Transform Infrared Spectra

Fourier Transform Infrared (FTIR) Perkin Elmer was used to investigate the structure of the DEaqs and DEpowd as well as to analyze their functional groups. The powdered *D. esculentum* leaves were used to investigate the DEaqs structure because the solution form will only result in water spectra. A potassium bromide (KBr) pellet was prepared by using the sampling device. Approximately 5 mg–10 mg of the sample powder and 90 mg–95 mg of KBr were blended, triturated, and mixed for 5 min using an agate mortar and pestle. The mixture was transferred to the IR sampling device and compacted via IR hydraulic press for 60 s. The KBr pellet was placed in the FTIR window and scanned by taking a blank spectrum. After completing the blank spectrum, the KBr pellet was removed from the window, thinly coated with the test sample, and then placed again in the FTIR window to measure the spectrum of the sample (Shatat, 2003; Pal et al., 2006).

3.4.4 Elemental Analysis

The constituents in *D. esculentum* leaves were analyzed using the CHNS/O Elementar Vario Macro Cube-Germany. Approximately 2000 mg of fine-cut, dried *D. esculentum* leaves were placed in a tin capsule and crimped. Three types of crimped capsules were placed in the autosampler for the CHNS/O analyzer (blank,

standard sulfamethazine, and *D. esculentum* leaf samples). The temperature of the analyzer oxidation was set to 1000 °C. Analysis was conducted automatically by a computer program, and the results were expressed in percentage.

3.5 Jar Test

The coagulation–flocculation experiments via jar test were performed in the laboratory by using a conventional jar test apparatus (VELP-Scientifica, Model: JLT6, Italy) with six 1 L cylindrical beakers. Stirring was performed mechanically using impellers equipped with 2.5 cm × 7.5 cm rectangular blades. The time and speed for the rapid and slow mixing were set using an automatic controller.

PACl was used as a chemical coagulant to evaluate and compare the efficiency of the natural coagulants using DEaqs and DEpowd as primary coagulant and coagulant aid. The samples were removed from the cold room and left for about 2 h at ambient temperature as described in Sections 3.2.1 and 3.2.2. The beakers were used for each experiment were filled with 500 mL of the leachate sample.

The coagulant was added into the beakers and the pH values were immediately adjusted to the desired values by adding appropriate amounts of H_2SO_4 and NaOH solutions. Given that different wastewater samples required various concentrations of H_2SO_4 and NaOH, 3 M H_2SO_4 and 3 M NaOH were used to adjust the pH for the leachate samples. The pH was measured using an HACH pH meter.

The coagulant aids were dosed after they were rapidly mixed. After the settling period, the supernatant was withdrawn from the beaker using a plastic

syringe from 2 cm below the liquid level for analysis (Ghafari et al., 2010; Aziz et al., 2007b; Tatsi et al., 2003). SS, colour, COD, turbidity, and NH_3-N of the samples were determined before and after the treatments. The analyses were performed in triplicates. Figure 3.4 shows the three phases of the jar test experiments conducted in this study.

Operating conditions for the jar test were established based on the mixing techniques, which included the intensity of rapid and slow mixing as well as the duration for rapid mixing, slow mixing, and settling. Following Awang and Aziz (2012) and Daud (2008), the experiments were performed at a fixed pH level of 6 and at 1000 mg/L doses of PACl, DEaqs, and DEpowd at both leachate samples. The optimum conditions were assessed based on the efficiency of the coagulants in removing SS, COD, colour, and NH_3-N from the samples. The efficiency of coagulants in removing turbidity was not considered because SS removals already reflected the removal pattern for turbidity.

The following experiments were performed in triplicate to determine the operating conditions:

I. Determination of the optimum rapid mixing time (T_R)

II. Determination of the optimum rapid mixing speed (ω_R)

III. Determination of the optimum slow mixing time (T_S)

IV. Determination of the optimum slow mixing speed (ω_S)

V. Determination of the optimum settling time (T_{SET})

The operating conditions from Phase 1 were used for Phase 2 to achieve the maximum optimum removal of parameters. Floc size measurements were performed in Phase 3 at an optimum pH level and a certain dose of PACl, and by using DEaqs as coagulant aid to overcome the expensive cost of floc measurement. The optimum conditions of PACl obtained from Phase 1 were used in the Phase 3 experiments.

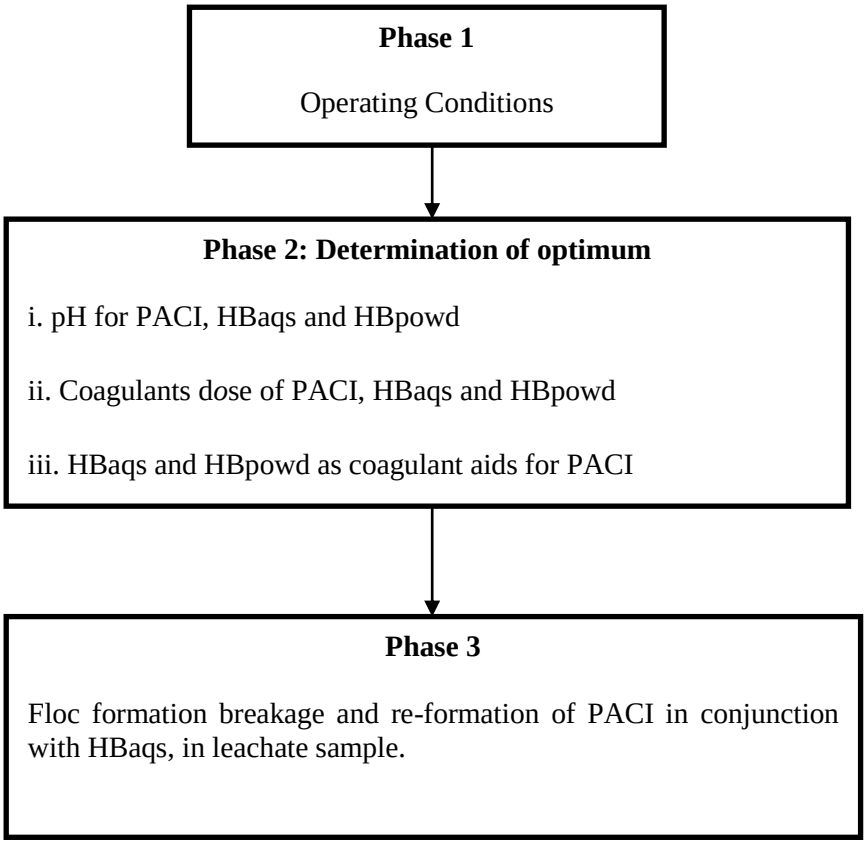

Figure 3.4: Phases in jar test study

3.6 Analytical Procedures

The samples were analyzed before and after each treatment. All procedures were performed in accordance with the Standard Method for the Examination of Water and Wastewater (APHA, 2005). The REs of SS, colour, COD, turbidity, and NH_3-N were measured using Equation 3.4.

$$\text{Removal Efficiency (RE) (\%)} = [(C_i - C_f) / C_f] * 100 \quad (3.4)$$

Where, C_i and C_f are the initial and final concentrations of sample, respectively.

The CA of the coagulants was analyzed using Equation 3.5, where RT_S refers to the residual parameter measured after settling, and RT_B refers to the residual parameter measured after settling with no coagulant as a blank (Okuda et al., 2001b; Antov et al., 2009; Šćiban et al., 2009).

$$\text{Coagulation Activity (CA)} = (RT_B - RT_S) / RT_B \quad (3.5)$$

Equation 3.5 does not have any unit. Compared to Equation 3.4, the values obtained by using Equation 3.5 represent the removal of parameters by coagulant and are not influenced by other factors such as chemical precipitation, especially when the experiment is performed under high pH.

3.6.1 Suspended Solids (SS) (Method: APHA 2540 D)

DR 2800 HACH spectrometer was used to determine the value of SS in mg/L. The measurement was taken at 810 nm wavelength.

3.6.2 Colour (Method: HACH- Platinum-Cobalt (PtCo) Standard Method based on APHA 2120 C)

Spectrophotometer DR 2800 was used to measure the true colour of concentration. The measurement was taken at 455 nm wavelength. In this method, the suspended solids and turbidity were filtered using 0.45µm filter paper. The deionized water was used as the blank sample.

3.6.3 Chemical Oxygen Demand (COD) (Method: APHA 5220 B)

COD was measured using Spectrophotometer DR2800 using calorimetric method at 620nm wavelength. COD reagent and COD reactor were used in this test. Sample (leachate) and blank solution (deionized water) will be added into the vial that contains COD reagent and heated for 2 hours using COD reactor at constant temperature of 110 °C. Samples were left for 1 hour to cool down at room temperature and measurement was done using DR 2800.

3.6.4 Turbidity (Method: APHA 2130B)

Turbidity measurement was carried out by using Turbidimeter model HACH 2100P with Nephelometric Turbidity Units (NTU). At first, turbidimeter was calibrated. Then, the samples that need to be tested were inserted into the turbidimeter. Finally, the values were noted.

3.6.5 Ammonia nitrogen (NH_3-N) (Method: APHA 4500 NH_3 C)

NH_3-N was measured directly from DR2800 in mg/L NH_3–N unit. The measurement was done at 425 nm wavelength. Deionized water was used as blank.

3.6.6 pH (Method: APHA 4500-H^+ B)

The pH value was determined by using an HACH pH meter. The readings were taken three times before they were averaged. Three buffer solutions, pH 4, pH 7, and pH 10, were used to calibrate the pH meter before pH was measured.

3.6.7 BOD_5 (Method: APHA 5210 B)

A leachate sample was pipetted into a BOD bottle containing aerated dilution water. The DO content was determined and recorded, and the bottle was incubated in the dark for five days at 20 °C. Final DO content was determined after five days, and the difference between final and initial DO readings was calculated. The decrease in DO was corrected for the sample dilution to represent the biochemical oxygen demand of the sample.

3.6.8 Heavy Metal Elements (Zinc, Copper, Iron, Manganese and Nickel)

Elements in the leachate samples were analyzed by using Agilent 7500 Inductively Coupled Plasma–Mass Specrometry. The samples must be filtered and acid-preserved before the analysis to avoid any interference. The above mentioned

instrument measured the ions produced by a radio-frequency inductively coupled plasma.

The analyte species originate from a liquid were nebulized, and the resulting aerosol was transported into the plasma torch by argon gas. Ions that were produced by high temperatures were entrained in plasma gas, extracted through a differentially pumped vacuum interface, and then separated by a mass spectrometer on the basis of their mass-to-charge ratio. Ions that were transmitted through the mass spectrometer were quantified by a channel electron multiplier or a Faraday detector, and the ion information was processed by the data handling system of the instrument.

3.6.9 Temperature, Electrical Conductivity (EC) and Oxidation-Reduction Potential (ORP)

These parameters were measured at sampling sites by using YSI 556 Multi Probe System. The measurement unit of temperature, EC and ORP were °C, mS/cm and mV, respectively.The readings were taken three times and averaged.

3.7 Floc Formation, Breakage and Reformation

A macroscopic floc strength test was performed to measure floc strength in terms of floc formation, breakage, and reformation. The test method was adopted and modified from Wei et al. (2010), Wang et al. (2009), and Jarvis et al. (2005). Floc formation, breakage, and reformation in the leachate samples were investigated by

using PACI as a coagulant and DEaqs as a coagulant aid at optimum mixing time and speed, pH level, and dosage.

The suspension was stirred at optimum rapid mixing speed and time as determined in Phase 1 of the jar test followed by slow mixing. Breakages were observed after increasing the stirring rate to 300 rpm for 2 min after the floc formation period. After the breakage period, the optimum slow stirring speed of 20 rpm was reintroduced for an additional 5 min to reform the flocs. Floc size was measured after slow mixing was introduced.

Flocs size was determined using the Malvern 2000-S Master Sizer in accordance to the method described by Jarvis et al. (2005). The instrument measures the particle size by passing a laser beam through a suspension of particles. A floc sample of about 10 mL was slowly taken from the flocculation vessels using a hand pippette and poured gently into a stirring vessel reservoir of the Malvern Master Sizer, which contained 700 mL of ultrapure water as a dispersion medium. Then, the suspension was constantly flowed through the instrument during the measurement cycle. The reservoir that held the sample dispersant was equipped with a stirrer and a pump to keep the sample in suspension as well as repeatedly circulate the sample and dispersant throughout the cell. The sample was stirred at a speed of 70 rpm (low velocity) by a two-blade stirrer to avoid floc breakage. It is important to ensure that the suitable speed was used for the measurement in order to avoid the breakage of the flocs due to the highly fragile and delicate flocs structure. This is because, the impact from the mechanical stirring can disintegrates the flocs into a finer structure (Sochan et al., 2014). Then the laser intensity was standardized at 77.8% intensity in order for the instrument to run. If the light intensity is less than 50%, the instrument needs to

be cleaned again until it reached the required intensity. After setting up the measurement, the sample was ran. The light intensity recorded on detectors is converted into particle size distribution (Sochan et al., 2014). Mean size ($D_{0.5}$) was used to denote particle floc size (Wang et al., 2009). Instead of all the precautions methods applied, it is very difficult to make sure that this procedure do not damage and break the floc particles at all, however, measurement of flocs particle size using Malvern Mastersizer in constant flow of the suspension through the instrument is said to be the less destruptive method (Jarvis et al., 2005)

According to previous studies (Wang et al., 2009; Yukselen and Gregory, 2004), the breakage and reformation of flocs were indicated by a 'strength factor' and 'recovery factor'. With this terminology, the two factors (%) are defined by using Equations 3.6 and 3.7 respectively.

$$\text{Breakage factor} = [\text{Size}_2 / \text{Size}_1] \times 100 \quad (3.6)$$

$$\text{Recovery factor} = [\text{Size}_3 / \text{Size}_1] \times 100 \quad (3.7)$$

Size_1, Size_2 and Size_3 are the flocculation index of initial, broken and re-formed flocs, respectively. A larger value of strength factor indicates that flocs are stronger than the flocs with a lower factor. Likewise, the floc with a larger factor shows better regrowth after high shear.

3.8 Sediment Percentage

The SP experiment was performed to determine if reducing the volume of used PACl from its optimum value could benefit floc/sludge reduction. Such effect must be determined because sludge production during treatment will increase the cost of sludge handling. Only the leachate samples from KSLS were used to test the SP of flocs formed by the coagulants because the leachate samples from KLS produced an insufficient amount of sludge after the coagulation–flocculation process.

Additional tests were performed by using PACl and DEaqs as coagulant aids in the KSLS leachate sample. The insignificant presence of flocs and highly coloured leachates after the treatment with DEaqs and DEpowd as primary coagulants resulted in confusing sludge volume observations. Therefore, the SP experiments were performed without using DEaqs and DEpowd as primary coagulants.

SP denotes the ratio between the volumes beneath the supernatant–suspension interface after 60 min of sedimentation (V_{60}). V_0 represents the initial leachate volume as expressed in percentage. V_0 is a measure of the sludge volume as calculated by Equation 3.8 (González et al., 2007; Daud, 2008).

$$SP\ (\%) = [\quad 1 - (V_{60} - V_0 / V_0)]\quad X\ 100 \tag{3.8}$$

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter summarizes all the research findings and discussions. The performance of *D. esculentum* leaf extracts as an alternative sole coagulant was first examined prior to its application as coagulant aid. The coagulating performance of these materials is also compared with that of PACl, a chemical coagulant. The characteristics of the raw landfill leachates from KSLS and KLS as well as those of *D. esculentum* as natural coagulant are also outlined in this chapter.

4.2 Leachate Characterization

Detailed characteristics of leachate sample collected from KSLS and KLS are given in Table 4.1.

The pH values varied at 6.87-8.42 and 7.99-8.89 for KLS and KSLS, respectively. Generally, the pH of a stabilized leachate is higher than that of a young leachate. The difference could be due to the stabilized leachate that is produced after or during the fermentation of methane; hence the pH is higher than 7.5 (Poznyak et al., 2003). The pH values remained within the permissible limit (6.0-9.0) set in the Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009, Malaysian Environmental Quality Act 1974 (Act 127) (Aziz et al., 2010; Aghamohammadi et al., 2007; Aziz et al., 2007b).

Table 4.1: Characteristics of raw landfill leachates at KLS (26 samples) and KSLS (26 samples) from October 2010 to November 2012

No.	Parameter	KLS (18 years)		KSLS (13 years)		Standard
		Range	Average	Range	Average	Discharge limit[a]
1	pH	6.87 – 8.42	7.81	7.99 – 8.89	8.30	6.0 – 9.0
2	EC (mS/cm)	1.80 – 3.54	2.59	3.43 – 22.62	14.20	-
3	ORP (mV)	-75 - +216.2	-5.4	-84.9 - +98.1	-24	-
4	Temperature (°C)	29.3 – 32.1	30.4	27.3 -37.6	35	40
5	Particle Size (d.nm)	588.1-851.3	691.4	317.7-390.7	346.5	
5.	Zeta Potential (mV)	-24.2 - -14.3	-20.4	-21.9 - -14.5	-19.1	-
6.	Turbidity (NTU)	40.3 – 178	88.9	25.2 - 235	124	-
7.	Colour (Pt Co)	134 – 960	275	1939 - 4388	3144	100
8.	SS (mg/L)	65 – 225	125	152-501	306	50
9.	BOD_5 (mg/L)	2.3 – 69	13.5	74.5 - 449	162	20
10	COD (mg/L)	85 – 580	231	590 - 1117	995	400
11	BOD5/COD	0.02 – 0.07	0.04	0.10 – 0.50	0.18	-
12	Ammonia-N, NH3-N (mg/L)	108 – 730	249	410 - 2160	1296	5.0
13	Copper (mg/L)	0.01 – 0.07	0.04	0.001 – 0.13	0.04	0.2
14	Iron (mg/L)	0.02 – 2.40	0.6	0.02 – 2.36	0.6	5.0
15	Manganese (mg/L)	0.03 – 0.14	0.09	0.002 – 0.231	0.08	0.2
16	Nickel (mg/L)	0.01 – 0.09	0.05	0.004-0.232	0.05	0.2
17	Zinc (mg/L)	0.005 – 0.35	0.09	0.02 – 0.23	0.12	2.0

[a] Environmental Quality (Control of Pollution from Solid Waste Transfer Station and Landfill) Regulations 2009 (ILBS, 2014)

During methanogenic stage, concentrations of heavy metals were lower as the solubility of inorganics was lower at high pH (Worrell and Vesilind, 2012; Ntampou et al., 2006; Tatsi and Zouboulis, 2002). This is in agreement with the findings of this study which showed that the concentration of copper, iron, manganese, nickel and zinc was less than 1 mg/L at both sites. Moreover, the lower concentration of metals in both sites is mainly due to adsorption and precipitation reactions, which in turn, are enhanced by the gradual increase in ORP values with increasing age of landfill (Lo, 1996). According to Table 4.1, the maximum values of ORP for leachate at KLS and KSLS were +216.2 and +98.1 mV, respectively, while the minimum values were -75 and -84.9 mV, respectively. This was in line with previously published data which showed the increase in the ORP values from negative to positive for fresh and old leachate samples respectively from Thessaloniki, Greece (Tatsi and Zouboulis, 2002).

Lower contents of heavy metals also contributed to lower electrical conductivity. The electrical conductivity recorded at KLS and KSLS were 3.54 and 22.62 mS/cm, respectively. The high values of leachate conductivity reflect the large content of soluble inorganics in landfill leachate (Tatsi and Zoubolis, 2002). Mixture of these low concentrated metals could cause acute detrimental impacts on living organisms (Nordberg, 2007). As can be seen in Table 4.1, KLS leachate sample having particle size of 691.4 d. nm which was much higher than that of KSLS (346.5 d. nm). Meanwhile, temperature for both landfill sites is within the allowable limit.

NH_3-N is a major toxicant to living organisms (Kamaruddin et al., 2013; Bashir et al., 2010; Kurniawan et al., 2006). For NH_3-N, ranges of 108-730 and 410-2160 mg/L were obtained for the leachate collected from KLS and KSLS,

respectively.Typical NH_3-N values of 6-430 mg/L were explained for methane fermentation phase (Kostova, 2006). In another literature, Li and Zhao (2002) reported that ammonia-N in stabilized leachate might range between 3000-5000 mg/L. As a result, the concentration of NH_3-N increases with the increase in age of the landfill which is due to the biodeterioration of protein and other nitrogen-containing organic matters. The high content of ammonia-N is the main factor that enhances algal growth; promote eutrophication due to decreases of dissolved oxygen (Kurniawan et al., 2006). In nature, diminishing NH_3-N concentration to safe level could take decades (EPA, 2000).

The zeta potential of leachate for KLS and KSLS without pH adjustment was -20.4mV and -19.1mV, respectively. The zeta potential value was much higher than -46mV and -32.6mV reported by Al-Hamadani et al. (2011) and Awang (2011), respectively. Based on colloid stability level (Table 2.6) and coagulation degree (Table 2.7) proposed by Sympatec GmbH (2009) and Shammas (2005), respectively, colloidal particles in KSLS and KLS were in incipent stability and coagulation activity was low in leachate.

Turbidity of leachate ranged from 40.3-178 and from 40.3-235 NTU for KLS and KSLS, respectively. The leachate at KSLS contained higher turbidity than that at KLS due to the landfill age and stabilization of leachate. Typical SS values of 200-2000 and 100-400 mg/L were recorded for the new (less than two years) and mature landfills (more than 10 years), respectively (Tchobanoglous et al., 1993). The SS value for both sites in this study was greater than high concentration of the permissible Malaysian standard level (50 mg/L). The high concentration of SS and

turbidity could be attributed to the presence of high organic and inorganic solids in both sites.

The maximum values of colour at KLS and KSLS were 960 and 4388 Pt Co, respectively, while the minimum values were 134 and 1939 Pt Co, respectively. The leachate at KSLS contained higher concentration of colour compared with that at KLS. According to the observation in this study, KSLS exhibited high intensity colour compared to KLS. This is due to the presence of high organic matters (measured as COD) associated with suspended solids and turbidity as shown in Table 4.1. However, there is no specific standard for acceptable colour concentration of landfill leachate before being discharged into water courses especially in Malaysia.

This study shows that pollutant concentrations in KSLS were higher than those in KLS. The high concentration of COD in KSLS indicated that the leachate contained a low concentration of volatile fatty acids and large amounts of fulvic and humic substances. A decrease in BOD_5 and COD is often reported with an increase in age of a landfill. KLS demonstrated low biodegradability (BOD_5/COD=0.04) compared to KSLS (BOD_5/COD=0.18). KLS and KSLS are considered as stable (methanogenic conditions) with high concentrations of COD and ammonia-N and low BOD_5/COD ratio.

4.3 Characteristics of *Diplazium esculentum*

The coagulant was characterized to provide a basic understanding of its chemistry and effectiveness in removing both particulate and organic materials. Understanding the chemistry of coagulants in terms of their acidity, solubility, active metal content, anion content, and speciation can help explain the differences among

their performances (Sinha et al., 2004). Therefore, the basic properties of *D. esculentum* leaves must be determined. The characteristics of these leaves are discussed in the following sections.

4.3.1 Isoelectric Point

Figure 4.1 shows the zeta potential of DEaqs and DEpowd as a function of pH. DEpowd has a negative surface charge over the same pH range . In contrast, at pH 4 (IEP), surface charge of DEaqs was absolutely neutral while it turned positive at pH below 4 and negative at pH above 4. Otherwise, DEpowd had negative surface charge over the same pH range.

The magnitude of the zeta potential indicates the potential stability of a colloidal system. If all the particles in a suspension have a large negative or positive zeta potential, then they will tend to repel each other and no tendency for the particles to come together will occur. However, if the particles have low zeta potential values, then no force will prevent the particles from coming together and flocculating. Deviation of zeta potential from zero to optimum coagulation conditions indicates other coagulation mechanisms surmount the coagulation process, not charge neutralization (Eikebrokk, Juhna and Østerhus, 2006). Thus, it can be said that both DEaqs and DEpowd were anionic polyelectrolytes and the major mechanism governing the aggregation of the constituents was bridging.

This is in agreement with Zhang et al. (2010), where the addition of anionic flocculant, TJ-FI (produced by *Proteus mirabilis* from a mixed activated sludge) aroused the negative zeta potential of kaolin clay suspension. That resulted in

increased static repulsive forces among the particles suggesting that bridging was the major mechanism involved and not charge neutralization.

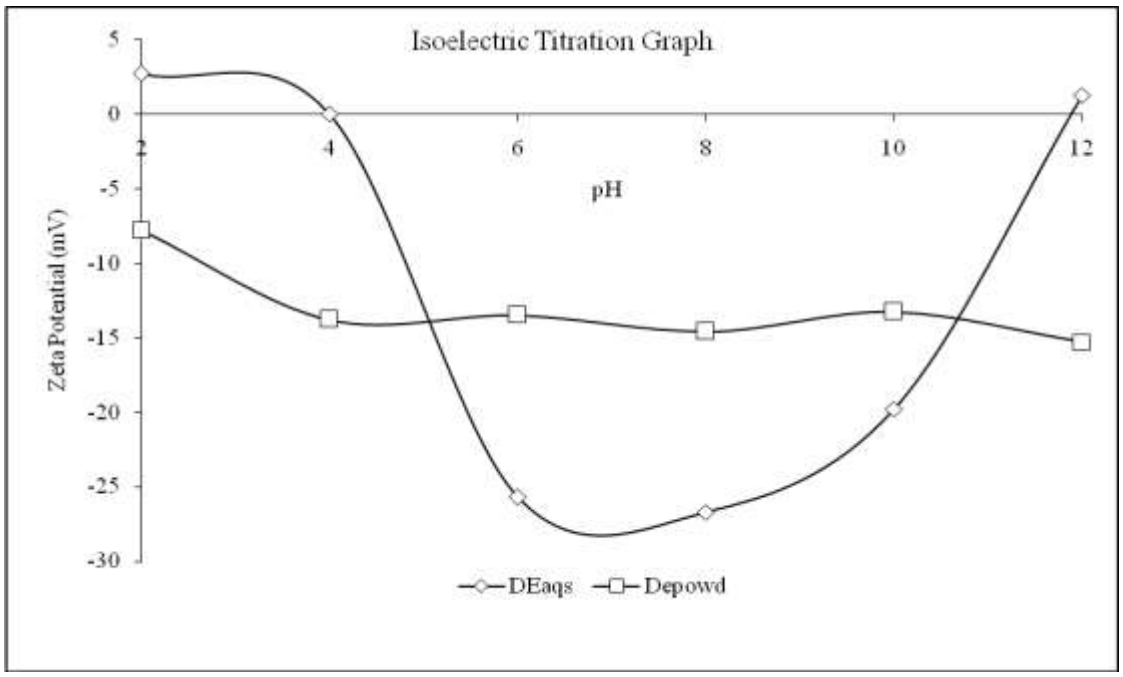

Figure 4.1: Variations of the zeta potential with respect to pH for DEaqs and DEpowd (100 mg/L)

4.3.2 Molecular Weight

Molecular weight is the most important characteristic of polymers in coagulation–flocculation processes. This characteristic can also greatly influence the effectiveness of the bridging mechanism (Basaran and Tasdemir, 2014). Molecular weight may range from a few thousand up to tens of millions.

The molecular weight of DEaqs and DEpowd in this study was approximately 221 and 275 kDa respectively (Figures 4.2 and 4.3). Zhang et al. (2010) and Beltràn-Heredia and Sànchez–Martin (2009) considered a molecular weight of over 100 kDa

as high molecular weight, it can be concluded that both DEaqs and DEpowd were a high molecular weight polymer. According to Bratby (2006), the bridging mechanism indicates that the increased molecular weight of a polymer should increase the efficiency of the flocculation because a longer chain should bridge more effectively, hence increasing the possibility of attaching these polymer segments with other particles and bridging them together.

Low molecular weights are expected to absorb rapidly because of their fast diffusion to the surface. Although polymer adsorption is irreversible, the desorption of polymer chains may occur in some cases. If the adsorption is irreversible, the chains with high molecular weight are not adsorbed. In contrast, if the adsorption is reversible, the chains with high molecular weight eventually displace the smaller adsorbed chains (Yarar, 2001).

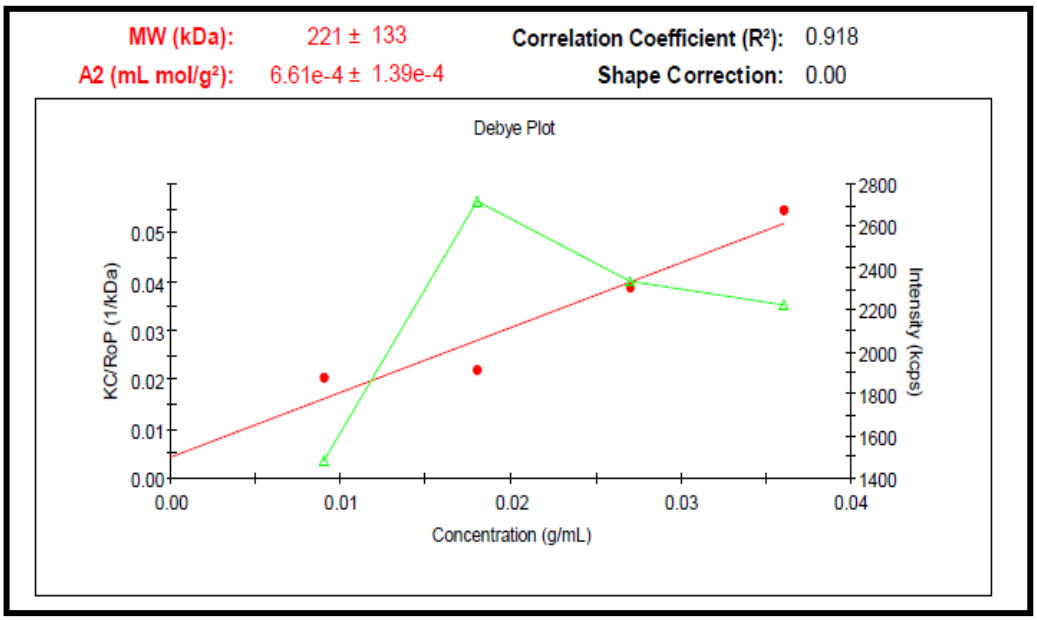

Figure 4.2: Debye plots for DEaqs

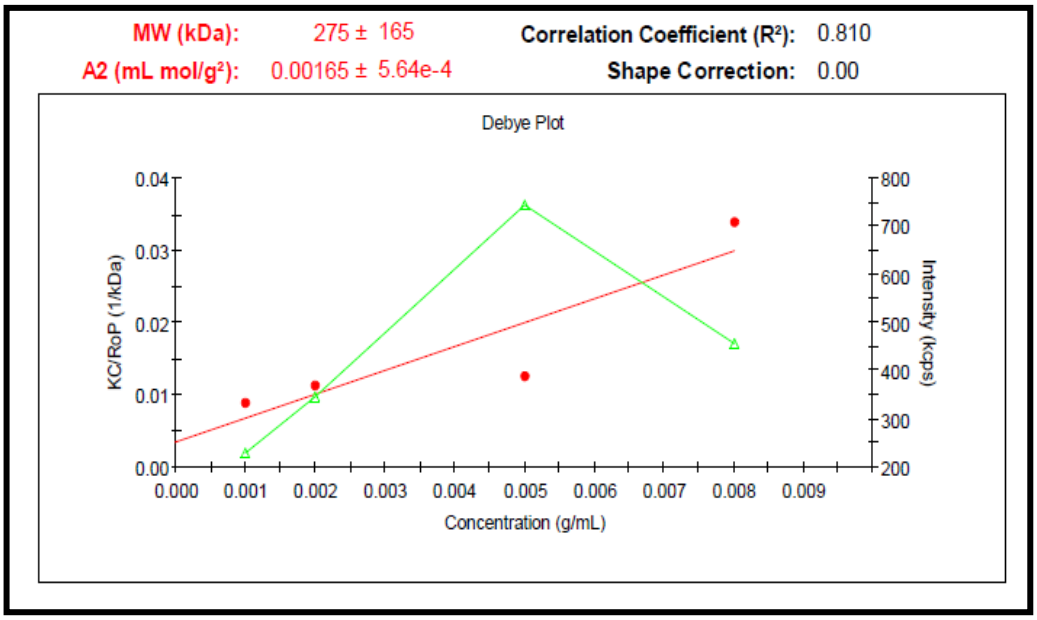

Figure 4.3: Debye plots for DEpowd

4.3.3 FTIR Spectrum

Generally, FTIR spectra analysis is a very important step in polymer characterization. FTIR is used for obtaining information about the chemical bonds in coagulants. However, FTIR spectrum is complicated. The bands might overlap or obscure one another and suggest more than a single functional group for a peak. The FTIR spectrum of DEpowd and DEaqs in the range of 4000-400 cm^{-1} is shown in Figure 4.4 and Figure 4.5, respectively.

Therefore, probable bond assignments of DEaqs and DEpowd FTIR peaks in Figure have been proposed in Table 4.2 based on various references available in literature (Guo et al., 2013; Zhang et al., 2013; CUBoulder Organic Chemistry Undergraduate Course, 2010; Li et al., 2008; Hanafiah et al., 2007; Prasertsan et al., 2006; Lu et al., 2005).

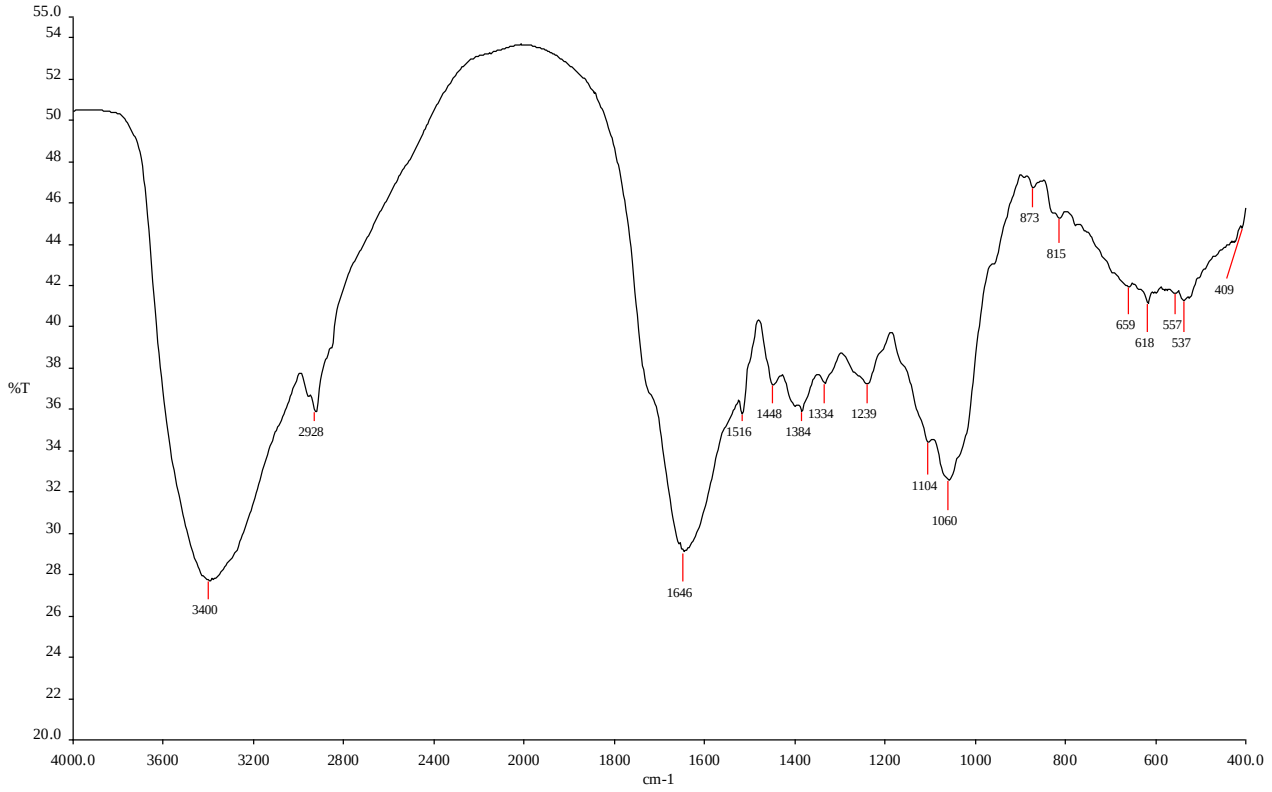

Figure 4.4: FTIR transmittance spectra of DEaqs

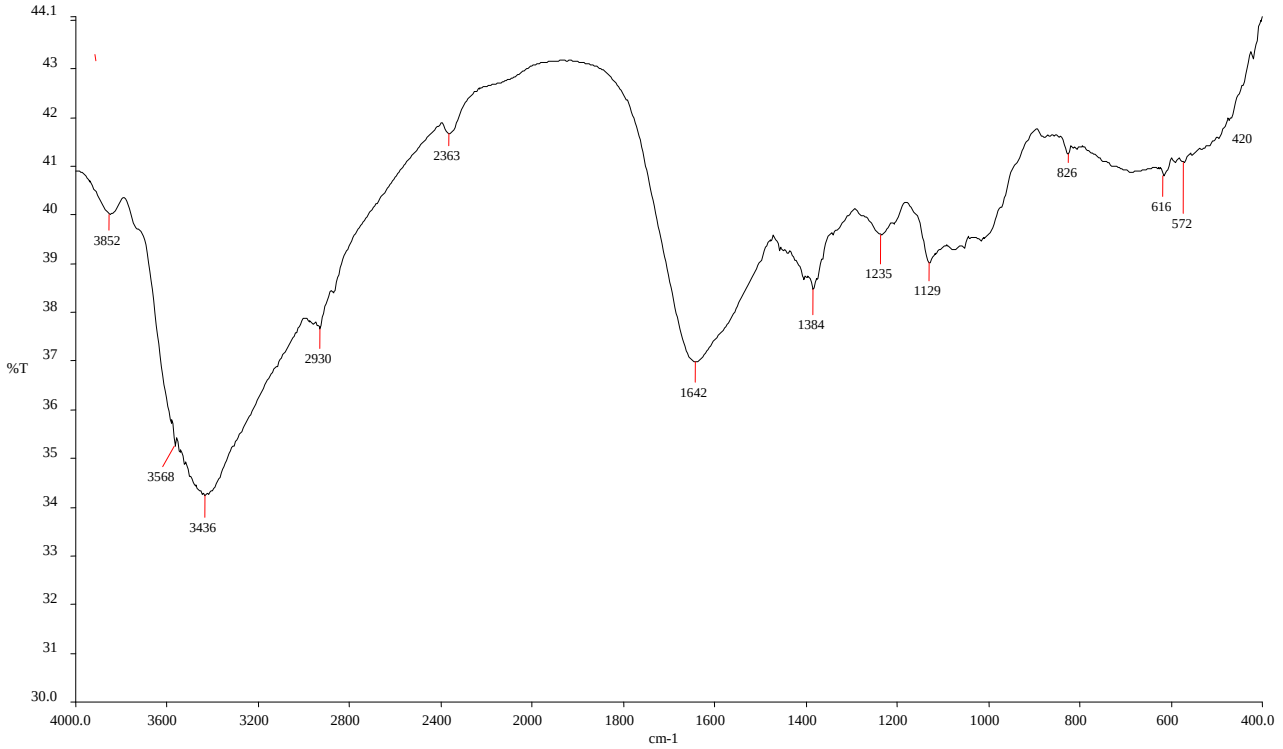

Figure 4.5: FTIR transmittance spectra of DEpowd

Table 4.2: Main functional groups of DEaqs and DEpowd

			FTIR peak (cm^{-1})	
Frequency range (cm^{-1})	Functional group	Bond assignment	DEaqs	DEpowd
3600 – 3100	Alcohols, phenols	H-bonded, O-H stretch	3400	3568 3436
3400-3250	1°, 2 ° amines, amides	N-H stretch	3400	-
3400-2400	Carboxylic acids	H-bonded, O-H stretch	3400	2930
1750-1625	Ketones	C=O stretch	1646	1642
1670-1600	Amides	C=O stretch	1646	1642
1650-1580	1° amines	N-H bend	1646	1642
1550-1450	Amines-secondary	N-H bend	1516	-
1335-1250	Aromatic amines	C-N stretch	1334	-
1320-1000	Alcohols, carboxylic acids,esters,ethers	C-O stretch/C-O-C	1239 1104 1060	1235 1129
910-665	1° , 2° amines	N-H wag	873 815	826

According to previous studies (Guo et al., 2013; Zhang et al., 2013; Zhang et al., 2010; Li et al., 2009; Liu et al., 2009; Lu et al., 2005; Kumar 2004), coagulation-flocculation effective groups like carboxyl, hydroxyl, amino (amine and amide) and methoxyl groups were detected in DEaqs and DEpowd. Hydroxyl (O-H) active group showed bands at 3400 cm-1 (DEaqs) and 3568, 3436, 2930 cm-1 (DEpowd) which most likely existed in functional groups like alcohols, phenols and carboxylic acids.

The absorption band at approximately 1642 cm^{-1}–1646 cm^{-1} is associated with the characteristic vibration of the C=O stretching of carboxyl active group in carboxylic acids and amides for both DEaqs and DEpowd. Absorption bands at 1060 cm^{-1}–1239 cm^{-1} (DEaqs) and 1129, 1235 cm^{-1} (DEpowd) are assigned to C–O stretching of alcohol groups. Amines in DEaqs showed peaks attributable to N-H bending (3400, 1516 cm^{-1}), strong C-N stretching (1334 cm^{-1}) and N-H wagging

(873, 815 cm^{-1}). Other than that, DEpowd lacking of N-H and C-N (stretching of amines) groups as compared to DEaqs even though both natural coagulant came from the same plant. N-H and C-N might be destroyed during the thiolation process of thioglycollic acid on hydroxyl groups of DEpowd.

The chemical structure of polymers consists of hydrocarbon backbone forming a long chain and the long chain carries active groups which can be anions, cations or no-ionic entities (Yarar, 2001). Figure 4.6 illustrated a polymer hydrocarbon backbone carries C=O groups reported by Yarar (2001), which is believed to be posed by DEaqs and DEpowd.

Hence, as depicted in Table 4.3, DEaqs and DEpowd will showed an anionic characters at high pH due to ionization of C=O groups. The dissociated carboxyl ($-C=O^{-1}$) groups will serves as ion bridge or binding sites for divalent metal cations ($Ca^{2+,}$ $Mg^{2+,}$ etc.) at the particle surface of leachate to induce the coagulation activity of DEaqs and Depowd.

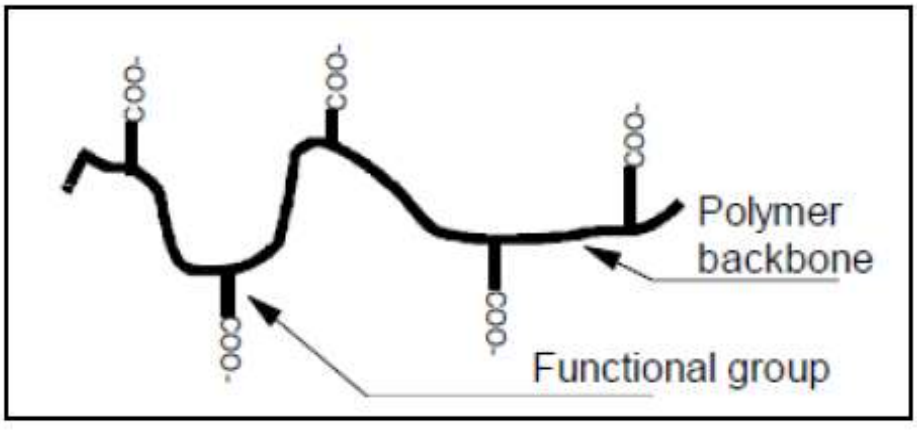

Figure 4.6: A typical polymer molecule consists of hydrocarbon backbone and attached functional group (Source: Yarar, 2001)

Table 4.3: Summary of the ionization properties of typical functional groups (Source: Yarar, 2001)

Active group	Name	Ionization properties
C=O-	Carboxyl	Ionized at pH 10, becomes $-(C=O)^{-}OH$ at low pH
$(C-O)NH-O^{-}$	Hydroxamate	Similar to carboxyl
NH^{3+}	Amine	Ionic at low pH, becomes $-NH^{2}$ at high pH
NH^{2}	Amide	Non-ionic at low or high pH
O	Ether	Non-ionic at low or high pH
OH	Alcohol	Non-ionic at low or high pH

4.4 Operating Conditions for Jar Test

Dosage of coagulant, pH and the other operational condition such as duration and speed of mixing are the important variables in coagulation-flocculation studies (Ghafari et al., 2010). As aforementioned in Section 3.5, the jar test was performed in this study to optimize seven variables in the following sequence: time and speed of rapid mixing, time and speed of slow mixing, settling time, pH, and coagulant dosage. The experiments were performed by following work done by Awang and Aziz (2012) and Daud (2008) which fixed pH level of 6 and at 1000 mg/L doses of PACl, DEaqs, and DEpowd at both leachate samples.

These operating variables were optimized for PACl, DEpowd, and DEaqs based on the highest removal of SS, colour, COD, and NH_3-N from the landfill leachates taken from KLS and KSLS. These variables were optimized by changing a

single factor and keeping the other factors unchanged for a particular set of experiments.

Table 4.4 summarizes the operating conditions for the landfill leachates as indicated in previous literature and this study. The strength of wastewater and the types of coagulants significantly affect the operating conditions for landfill leachates. However, such factors do not significantly change the operating conditions.

Table 4.4: Range of operating conditions in landfill leachates for metal salts or polyelectrolytes alone and metal salts in conjunction with polyelectrolytes obtained from literature and this study

No.	Coagulant (Sample)	Volume (mL)	T_R (min)	ω_R (rpm)	T_S (min)	ω_S (rpm)	T_{SET} (min)	References
1.	Hibiscus rosa sinensis leaf + Alum (PBLS)	500	3	200	20	30	30	Awang and Aziz, 2012
2.	Lateritic soil (PBLS)	200	3	100	10	30	30	Syafalni et al., 2012
3.	Psyllium husk, PACI, Alum (PBLS)	-	2	80	30	30	120	Al-Hamadani et al., 2011
4.	Alum, PACI (PBLS)	-	1	80	15	30	-	Ghafari et al., 2010
5.	Alum, PACI (PBLS)	500	1	150	20	20	30	Aziz et al., 2009
6.	Alum, Ferric chloride, Ferrous sulphate, Ferric sulphate (PBLS)	500	1	350	19	50	60	Aziz et al., 2007b

Table 4.4: Continued

No.	Coagulant (Sample)	Volume (mL)	T_R (min)	ω_R (rpm)	T_S (min)	ω_S (rpm)	T_{SET} (min)	References
7.	Alum, Ferric chloride	-	5	200	55	60	60	Tatsi et al., 2003
8.	Alum, Ferric chloride	500	3	200	15	40	-	Amokrane et al., 1997
9.	PACI							
	KSLS	500	3	200	20	30	30	
	KLS	500	3	150	10	20	30	
	DEaqs							This study
	KSLS	500	3	200	20	30	40	
	KLS	500	3	200	15	30	40	
	DEpowd							
	KSLS	500	4	250	20	30	40	
	KLS	500	4	250	20	30	40	

*PBLS= Pulau Burung Landfill Site, Penang, Malaysia

4.4.1 Effect of Rapid Mixing

Rapid mixing is required to distribute the coagulant species among the particles within the shortest time possible to increase the effectiveness of the destabilized colloidal particles as well as to promote the formation of floc particles (Davis and Cornwell, 2008; Bratby, 2006; Rivas et al., 2004).

Therefore, a short period of intense, turbulent mixing is desirable, and the coagulants must be added after sufficient mixing. A study of rapid mixing involves chemistry theories in coagulant chemistry, mixing, and mass transfer. Given the complexity of such theories, no simple and concrete guideline on rapid mixing can be offered.

According to Table 4.4, the time and speed of rapid mixing for PACl, DEaqs, and DEpowd were tested in a wide range (T_R = 1 min to 5 min and ω_R = 70 rpm to 300 rpm) to cover the time and speed that were applied in the previous studies. Thus, results obtained obviously show that contact time for PACI (3 min) was slightly shorter than DEaqs and DEpowd (4 min). Better performance can be achieved by adding the coagulant into both KLS and KSLS samples under high-intensity agitation. According to Bolto and Gregory (2007), high shear rates ensure that the coagulant molecules are homogenously distributed in the slurry. High shear rates that are associated with rapid mixing can also facilitate the transport of coagulant species and increase the adsorption rate. Therefore, an ultimate performance can only be achieved when the coagulants are fully dispersed during extended periods of high shear rates. However, the ineffective dispersion of a high concentration of coagulants at low shear rates may lead to poor flocculation performance.

High-intensity rapid mixing also helps overcome any electrostatic barriers by increasing the kinetic energy of the particles (Gray et al., 2007). A high shear rate produces an initial perikinetic phase that enhances the Brownian motion between colloids (Bouyer et al., 2001). Therefore, the flocs produced at high shear rates are larger than those produced at low shear rates, hence facilitating the separation processes (Gray et al., 2007).

4.4.2 Effect of Slow Mixing

Coagulation is usually followed by flocculation, a slow mixing technique that promotes the aggregation of destabilized (coagulated) particles. Therefore, slow mixing is a key aspect of the flocculation process. A slow mixing process must be

performed to enable the particles to approach one another and form larger agglomerations or flocs. The flocs continue to grow as they continue to colllide and interact with coagulants. In other words, a slow mixing stage affects the particle RE (Davis and Cornwell, 2008) as well as controls floc growth and structure (Bouyer et al., 2001). The water is stirred during the slow mixing process to encourage the floc particles clump together.

In this study, the range of variations for time and speed of slow mixing were set to T_S = 5 min to 30 min and ω_S = 10 rpm to 30 rpm respectively. Different slow mixing speeds were initially tested through a series of coagulation–flocculation experiments that apply the optimum values obtained from the aforementioned tests for rapid mixing time and speed (Section 4.4.1). Previous studies set the ω_S intensity between 15 and 60 rpm with the T_S varying from 10 min to 55 min (Aziz et al., 2009; Tatsi et al., 2003). Table 4.4 shows that the results for slow mixing speed (ω_S = 20 rpm to 40 rpm) and slow mixing time (T_S = 10 min to 20 min) in this study are consistent with the ranges reported in previous literature.

These results show that the slow mixing process is a time-dependent procedure that directly affects the clarification efficiency of measured parameters by allowing the suspended particles in the leachate to collide with one another through gentle and prolonged agitation. Lowering the mixing speed improves the removal of SS, colour, COD, and NH_3-N as well as subsequently reduces the shearing rate of flocs during the flocculation phase. The agitation must be performed thoroughly to encourage interparticle contact, but performed gently to prevent the disintegration of existing flocculated particles.

According to Jarvis et al. (2005), velocity gradient should have low intensity and contact time should be longer than that of the rapid mixing stage for the flocs to grow to their optimum size and strength. Stirring too fast can break large particles apart and subsequently restabilize the colloids, whereas stirring too slowly can prevent the particles from clumping.

4.4.3 Effect of Settling Time or Sedimentation

The settling process is performed to remove the suspended particles from the water. These particles include large solids that can be settled by gravity alone without external aids and nonsettleable materials that are often colloidal in nature. Therefore, settling without prior coagulation–flocculation results in the removal of relatively coarse SS. Table 4.4 shows that the settling period for DEpowd and DEaqs was slightly longer (T_{SET} = 40 min) than that for PACl (T_{SET} = 30 min) in the KLS and KSLS samples.

The floc quickly settled out within the first 10 min, and minimal changes were observed in their final values after 20 min. According to Tasdemir and Tasdemir (2012), a longer settling time may provide additional mixing time and subsequently increase the collision probability between particles and coagulants. The amount of time the water spends in this process is a key performance parameter. An adequate amount of time must be provided to generate particles that are large enough to be removed efficiently in the subsequent treatment processes.

Table 4.5 shows the removal percentages in each stage of the optimization process. These percentages are achieved to optimize each operating condition and to improve the treatment efficiencies of PACl, DEaqs, and DEpowd in the KLS and KSLS samples. The SS, colour, COD, and NH_3-N removal efficiencies of PACl, DEaqs, and DEpowd in the KLS sample were higher than their efficiencies in the KSLS sample because of the different characteristics of the wastewater used in this study (Ghafari et al., 2010; Anastasakis et al., 2009). DEaqs is expected to react more effectively compared to DEpowd in the KLS samples. Therefore, DEaqs exhibited favorable performance in wastewater with a low pollutant level.

Table 4.5: Percentage of removal in SS, colour, COD and ammonia-N achieved at the end of optimum operating conditions

Coagulant (Dosage)	Site	Step of Optimization	Removal (%)				Reference
			SS	Colour	COD	NH_3-N	
PACI (1000 mg/L)	KSLS	Time of rapid mixing (T_R) = 3 min Speed of rapid mixing (ω_R) = 200 rpm Time of slow mixing (T_S) = 20 min Speed of slow mixing (ω_S) = 20 rpm Settling time (T_{SET}) = 30 min pH = 6	82	79	16	28	Appendix B (1)
	KLS	Time of rapid mixing (T_R) = 3 min Speed of rapid mixing (ω_R) = 150 rpm Time of slow mixing (T_S) = 10 min Speed of slow mixing (ω_S) = 20 rpm Settling time (T_{SET}) = 30 min pH = 6	92	88	36	38	Appendix B (4)

Table 4.5: Continued

Coagulant (Dosage)	Site	Step of Optimization	Removal (%)				Reference
			SS	Colour	COD	NH_3-N	
DEaqs (1000 mg/L)	KSLS	Time of rapid mixing (T_R) = 3 min Speed of rapid mixing (ω_R) = 200 rpm Time of slow mixing (T_S) = 20 min Speed of slow mixing (ω_S) = 40 rpm Settling time (T_{SET}) = 50 min pH = 6	66	48	16	48	Appendix B (2)
	KLS	Time of rapid mixing (T_R) = 3 min Speed of rapid mixing (ω_R) = 200 rpm Time of slow mixing (T_S) = 15 min Speed of slow mixing (ω_S) = 30 rpm Settling time (T_{SET}) = 40 min	86	50	50	51	Appendix B (5)
(DEpowd (1000 mg/L)	KSLS	Time of rapid mixing (T_R) = 4 min Speed of rapid mixing (ω_R) = 250 rpm Time of slow mixing (T_S) = 20 min Speed of slow mixing (ω_S) = 30 rpm Settling time (T_{SET}) = 40 min pH = 6	72	23	28	29	Appendix B (3)
	KLS	Time of rapid mixing (T_R) = 4 min Speed of rapid mixing (ω_R) = 250 rpm Time of slow mixing (T_S) = 20 min Speed of slow mixing (ω_S) = 30 rpm Settling time (T_{SET}) = 40 min pH = 6	74	24	32	31	Appendix B (6)

4.4.4 Effect of Optimum pH and Dose on Operating Conditions

Given that landfill leachates have their own characteristics, researchers always try to determine the optimum dosage of coagulants according to their economic and efficient aspects. The effectiveness of the coagulation process greatly depends on the dosage of the coagulant and the pH of the leachate during the

process. However, the effectiveness of this process as well as the relationship among the leachate quality, coagulant dosage, and optimum pH level cannot be easily predicted because of the complex chemistry of the coagulation–flocculation process.

Table 4.5 reveals that the final removal for measured parameters was low due to the non-optimum dosage of coagulants and pH. Unlike the present study, Ghafari et al. (2010) performed experiments by using optimum dosage and pH, which affected the optimum operating conditions in such a way that the intensity of the velocity and time for rapid and slow mixing was decreased. Ghafari et al. (2010) set the optimum condition as T_R = 45 s and PACl dosage = 1900 mg/L at pH 7.5, whereas the current study set the optimum condition as T_R = 3 min and PACl dosage = 2000 mg/L at pH 6.

More hydrolysis products can be produced by using an optimum pH and dosage. Therefore, the charge neutralization process in this study only occurred within a short period. However, this study required a longer time to reach the same point that could be achieved using optimum pH and dosage. The same conditions were applied for rapid and slow mixing velocity. Therefore, the operating conditions must be tested at an optimum dosage and pH to save energy (electricity for the jar test) and time. Additionally, the stiring speed and time had a moderate positive influence on coagulation activity.

4.5 Optimum pH

As mentioned in Section 4.3.1, a zeta potential test was performed at different pH levels to determine the IEP for DEaqs and DEpowd. Theoretically, IEP or PZC should provide the best coagulation conditions as described briefly by Duan and Gregory (2003) based on aluminum hydroxide precipitation. Given that the IEP values of aluminum hydroxides have been extensively covered in extant literature, this study will only consider the provided IEP value. However, many complex factors are involved when dealing with the heterogeneous suspensions in water, and the zeta potential measurements do not always present a high value in operational circumstances (Tebbutt, 1983). Besides, the zeta potential only measures one aspect of the entire process and may not reflect all conditions that lead to coagulation efficiency (Bratby, 2006).

4.5.1 Effect of the Optimum pH for PACI

The pH influences the nature of the produced polymeric metal species that will be formed as soon as the metal coagulants are dissolved in water (Guo et al., 2010). The hydrolysis of metal ions occurs immediately after they are added in water, and PACl can rapidly form dissolved aluminum species or aluminum hydroxide precipitates, as well as significantly influence the coagulation process (Zhang et al., 2008).

Figures 4.7 and 4.8 present the percentage reduction and final concentration of PACl for removing SS, turbidity, colour, COD, and NH_3-N from the KLS and KSLS samples. To determine the optimum pH range, several experiments were

conducted using different pH values and a 1000 mg/L dosage of PACl in both KSLS and KLS samples. The pH effect was examined by adjusting the pH value of the leachate samples from both sites by using solutions of 3M sulfuric acid (H_2SO_4) and 3M sodium hydroxide (NaOH) between 2 and 12 for PACl.

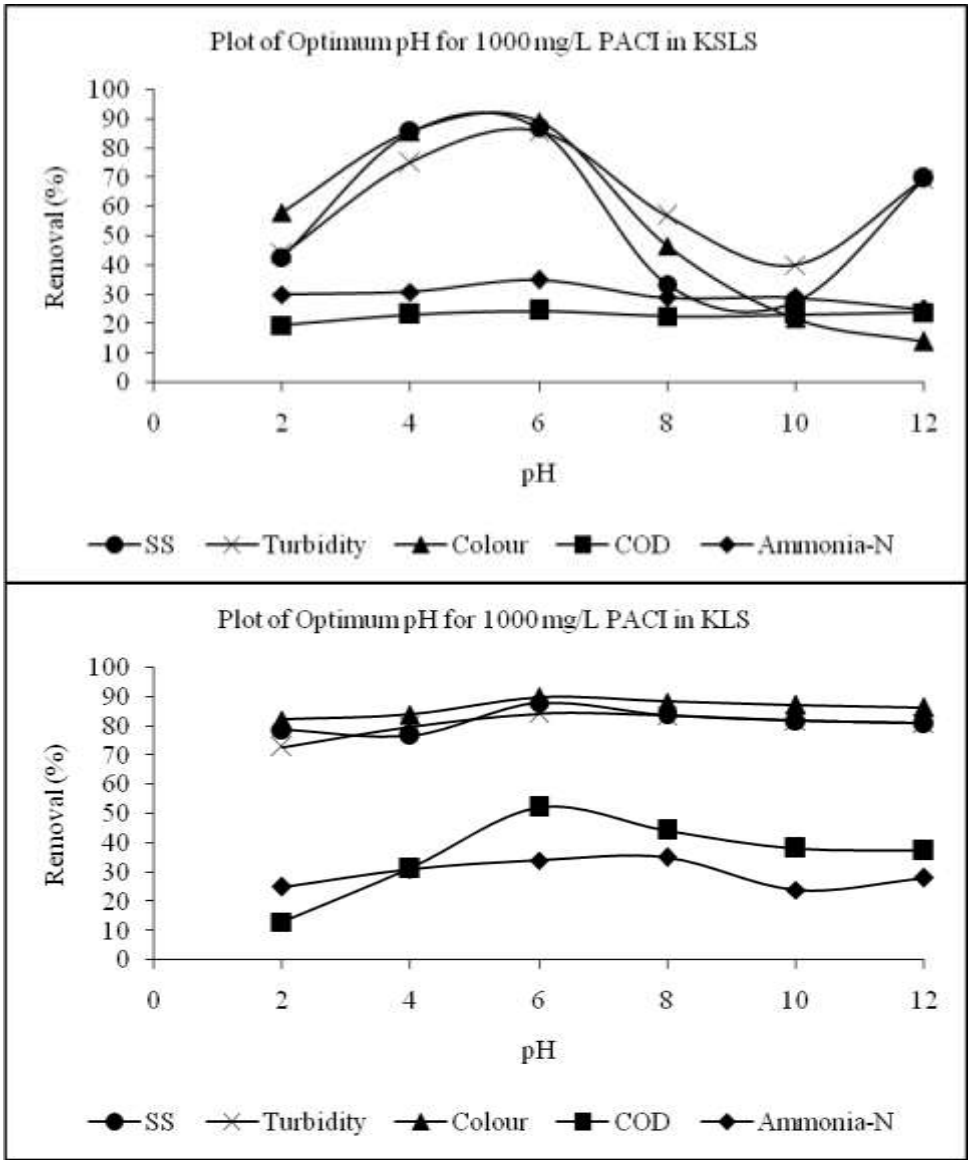

Figure 4.7: Percentage removal of SS, turbidity, colour, COD and ammonia-N vs pH of PACI in KSLS and KLS leachate

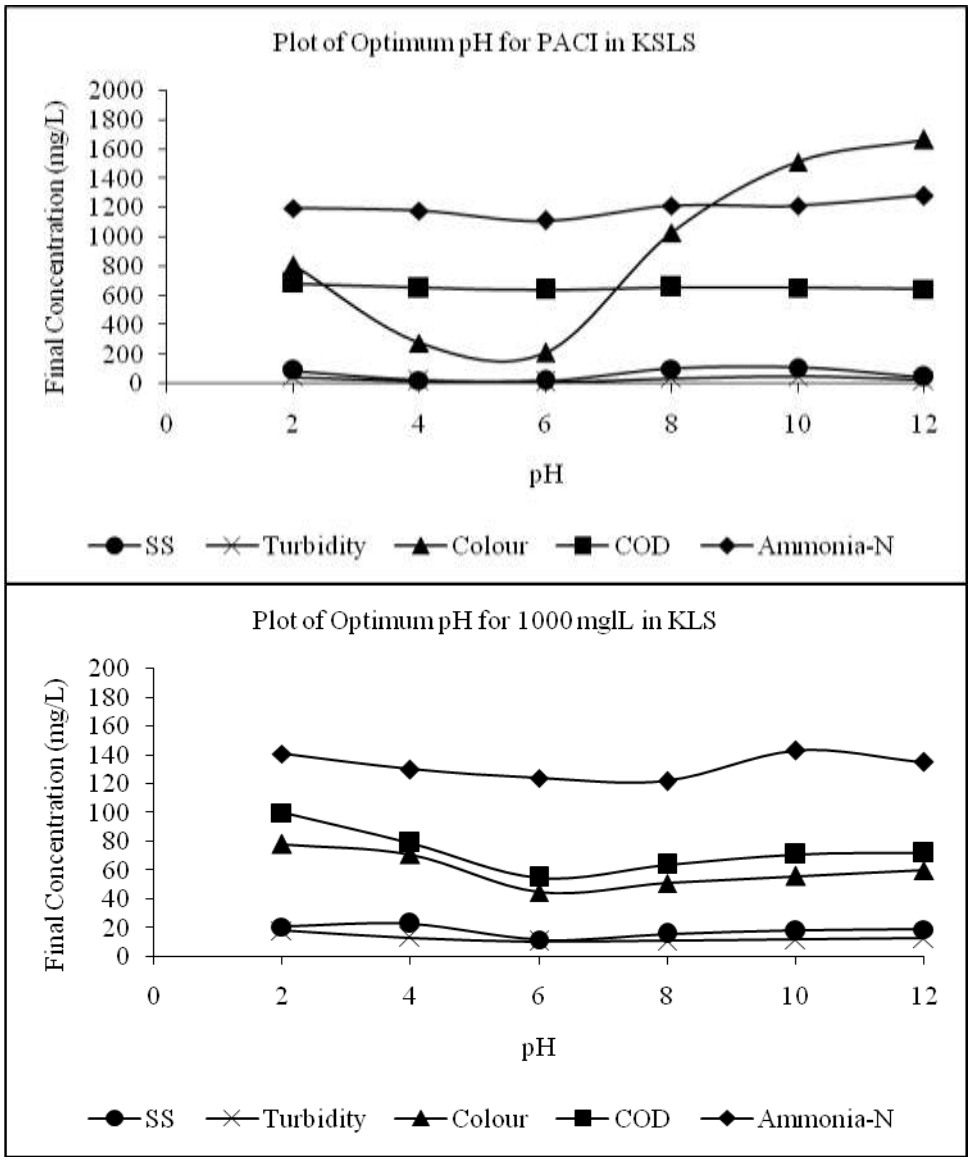

Figure 4.8: Final concentration of SS, turbidity, colour, COD and ammonia-N vs pH of PACI in KSLS and KLS leachate

The pollutants in both KSLS and KLS samples were removed by using PACl at pH 6. Appendix C (C (a) (1) and C (b) (1), respectively) shows detailed results on the removal of pollutants from the KSLS and KLS samples. Figure 4.7 shows that the removal curves of SS, turbidity, and colour substantially increased to pH 6 and decreased afterwards. The pH variations affected the removal of SS, turbidity, and colour from both the KSLS and KLS samples by over 80% at optimum pH. However, the removal rates for SS and turbidity in the KSLS landfill leachate sample suddenly dropped as the pH value gradually increased from 8 to 10 and then to 12. This behavior can be explained in terms of chemical precipitation. NaOH was used as an alternative hydroxyl ion to increase the pH to levels at which the precipitation of divalent metals (i.e., Ca^{2+} and Mg^{2+}) occurs. $CaCO_3$ normally precipitates at a pH range of 9.1 to 9.5, whereas Mg $(OH)_2$ precipitates at pH 9.5, becomes significant at above pH 10.5, and becomes complete at pH 11 to 11.5. $Mg(OH)_2$ precipitation (PZC approximately at pH 12.4) has a large adsorptive surface area as well as a positive charge to attract negative particles, including $CaCO_3$ flocs, induce adsorption, and promote agglomeration. The $CaCO_3$ precipitation (PZC approximately at pH 8 to 9) acts as a weighting agent by increasing the density of the settleable particles (sweep coagulation). Therefore, only the large particles are entrapped (Semerjian and Ayoub, 2003). This condition will reduce or neutralize the surface charge of the particles. Nevertheless, the removal of SS and turbidity at pH 12 is still lower than at optimum pH 6.

The high concentration of colour in the KSLS and KLS samples (Figure 4.8) indicated the presence of an increased content of organic matter in the leachate. The colour intensity gradually reduced from black to light yellow as the pH approached

the optimum value (pH 6). The acid medium (with pH values between 4 and 6) demonstrated the best color removal results. pH adjustment may change the ionization of the colour molecules and produce corresponding effects on bond lengths and configurations.

The removal of COD in the KSLS and KLS samples increased as the initial pH of the leachate increased from 2 to 6. However, COD removal remained constant and slightly decreased from pH 8 to 12 in both KSLS and KLS samples. This observation can be attributed to the fact that when the pH is higher than 8, the suspension system cannot be destabilized easily because the speciation of aluminum is transformed to $Al(OH)_4^-$. These ions reduce the COD through PACl because of the electrostatic repulsion between the negatively charged colloidal particles in leachate and $Al(OH)_4^-$ ions.

The NH_3-N removal in both samples was relatively low. At an optimum pH (pH 6), the highest removal percentages of PACl for SS, turbidity, colour, COD, and NH_3-N were 87%, 86%, 89%, 25%, and 35%, respectively, for KSLS and 88%, 84%, 90%, 52%, and 34%, respectively, for KLS. The optimum pH value in this study was not consistent with the results obtained by several authors in their leachate coagulation–flocculation experiments (Al-Hamadani et al., 2011; Ghafari et al., 2010; Aziz et al., 2009), where the optimum pH was set between 7 and 7.5.

Nevertheless, some other researchers (Choudhary et al., 2013; Jayashri et al., 2013; Yang et al., 2010) claimed that the optimum pH for PACl (for various wastewater types) ranges between 5 and 8. Therefore, instead of assigning a specific optimum pH value, ranges of pH values were used in this study for further

comparisons. The proposed optimum pH variation for PACl ranged between 5 and 8. Therefore, an optimal range of pH value can be used for a particular type of wastewater in which the coagulation process can effectively take place. Wider ranges of pH values depend on numerous factors, such as variations in the characteristics of wastewaters, as well as the type and concentration of coagulants (Banihashemi et al., 2008; Annadurai et al., 2004). Table 4.6 shows the optimum pH and dosage for PACl in various wastewaters.

Table 4.6: Comparison of Optimum pH and dose of PACI in various wastewaters

Reference	Wastewater	Measured Parameters	Optimum pH	Optimum Dosage (mg/L)
This study	Landfill leachate	SS, turbidity, colour, COD, ammonia-N	6	2000
Choudary et al., 2013	Paper mill	Adsorbable organic halides (AOX), chlorophenolics, chlorinated resin & fatty acids (cRFA), colour, COD	8	1500
Jayashri et al., 2013	River water	Turbidity	6.5-7.6	30
Al-Hamadani et al., 2011	Landfill leachate	COD, colour, SS	7.5	7200
Ghafari et al., 2010	Landfill leachate	TSS, turbidity, colour, COD	7.5	1900

Table 4.6: Continued

Reference	Wastewater	Measured Parameters	Optimum pH	Optimum Dosage (mg/L)
Yang et al., 2010	River water	Turbidity, UV_{254} absorbance, Dissolved organic carbon (DOC)	6	15
Aziz et al., 2009	Landfill leachate	Colour, COD, ammonia-N	7.5	2000

As discussed in Section 2.14.1, the coagulation mechanisms of metal coagulants include charge neutralization, precipitation, bridge aggregation, adsorption, and sweep flocculation. The coagulation mechanism is based on the destabilization of the colloidal structure, which subsequently allows aggregation and separation from the solution. The different mechanisms or the combinations of these mechanisms may become dominant under different conditions.

Several researchers found that the IEP for aluminum hydroxides falls between the pH range of 8 to 9 (Cañizares et al., 2009; Kosmulski, 2009a and 2009b; Bolto et al., 2001). The aluminum hydroxide is neutral at IEP, positively charged at below IEP, and negatively charged at above IEP (Zetasizer Nano User Manual, 2008; Kumpulainen et al., 2008). In other words, the precipitate becomes positively charged at low pH values and can neutralize the negative charge of particles in the water.

Primary aluminum hydrolysis products, including $Al(OH)^{2+}$, $Al(OH)_2^{+}$, $Al_2(OH)_2^{4+}$, and $(Al_3(OH)_4^{5+}$, are formed when the pH is lower than 5. These positive ions easily neutralize the negative charges of leachates and further destabilize them (Yang et al., 2011; Zhang et al., 2008). In contrast, PACl produces highly positively

charged polymeric metal hydroxyl species, such as $Al_{13}O_4(OH)_{24}^{7+}$ and $Al(OH)_3$, in the solution when the pH ranges between 6 and 8. The colloids are easily adsorbed and co-precipitated by these species, which have low solubility and large surface areas, hence maximizing the physical action of flocculation. These species neutralize the negative charges on the colloidal particles and facilitate agglomeration, which subsequently improves coagulation performance. This notion has been supported by Aguilar et al. (2005), who claimed that positively charged aluminum hydroxide species are predominant at pH values ranging between 4 and 6, whereas a pH range of 5.5 to 7.5 is ideal for the precipitation of $Al(OH)_3$. These results were also supported by Lin et al. (2008) and Chakrabarti et al. (2008), who argued that the hydrolysis products of aluminum are affected by the pH value of solutions.

pH can also affect the balance between the reactions of organic functional groups with hydrogen ions and the aluminum hydrolysis products (Yan et al., 2007). Under weak acid conditions, hydrogen ions can outperform the metal hydrolysis products for organic ligands. Therefore, the amount of organic ligands decreases, and the colloids and organic materials can be removed by metal salts (Yang et al., 2010).

Under alkaline conditions, the increased pH value favors the hydrolysis of PACl and decreases the amount of positively charged ions (Kim et al., 2001; Yang et al., 2011) because most aluminum species exist in the form of negatively charged $Al(OH)_3$ and $Al(OH)_4^-$ ions, which produce a weak charge neutralization effect. Therefore, the particle and organic materials cannot be removed efficiently. Bridge aggregation and adsorption may play highly effective roles in pollutant removal at a higher range of pH when treating landfill leachates.

The RE for measured parameters in both samples began from a pH range of 4 to 6. This result was in accordance with that of a previous study on the coagulation performance of PACl under different pH values during the treatment of water from the Yellow River. Turbidity RE increased along with pH, and could reach up to 85.7% at a dosage of 15 mg/L at an optimum pH value of 6. Therefore, the charge neutralization effect of PACl for landfill leachate under acidic conditions was superior to that under alkaline and neutral conditions. This result coincides with that of Li et al. (2010), who argued that coagulation–flocculation is most effective in a low pH range.

4.5.2 Effect of Optimum pH for DEaqs and DEpowd

Given that the factor of pH during coagulation affects the chemistry of the coagulant, the influence of landfill leachate pH on coagulation effectiveness must be determined. Figures 4.9 and 4.10 (see Appendix C (a) 2 to (a) 3 and (b) 2 to (b) 3, respectively) illustrate the effect of pH on coagulation effectiveness using DEaqs and DEpowd for a coagulant dosage of 1000 mg/L in the KSLS and KLS samples. Based on these graphs, the overall maximum percentage removal for both coagulants in both KSLS and KLS was observed at pH 10.

However, a considerable removal percentage was also observed under acidic conditions, particularly at a pH range of 2 to 4 and at a higher pH range of 11 and 12. This value can greatly fluctuate according to the class of pollutants and the matrix effect in complex leachates because the landfill leachate will have its own characteristics (Wang et al., 2002).

Previous studies report that the optimum pH for other natural coagulants, such as natural stone powder (Basaran and Tasdedemir, 2014), chestnut and acorn (Ŝćiban et al., 2009), *C. opuntia* (Zhang et al., 2006), *M. oleifera* (Okuda et al., 2001a and 2001b), and *P. juliflora* and *Cactus latifaria* (Diaz et al., 1999), must be set to 10. At an optimum pH of 10, the maximum removal percentage of DEaqs for SS, turbidity, colour, COD, and NH_3-N were 68%, 53%, 44%, 17%, and 55%, respectively, in the KSLS sample, and 70%, 83%, 51%, 56%, and 42%, respectively, in the KLS sample. In contrast, the removal percentage of DEpowd for SS, turbidity, colour, COD, and NH_3-N were 75%, 67%, 40%, 41%, and 36%, respectively, in the KSLS sample, and 79%, 80%, 37%, 36%, and 31%, respectively, in the KLS sample.

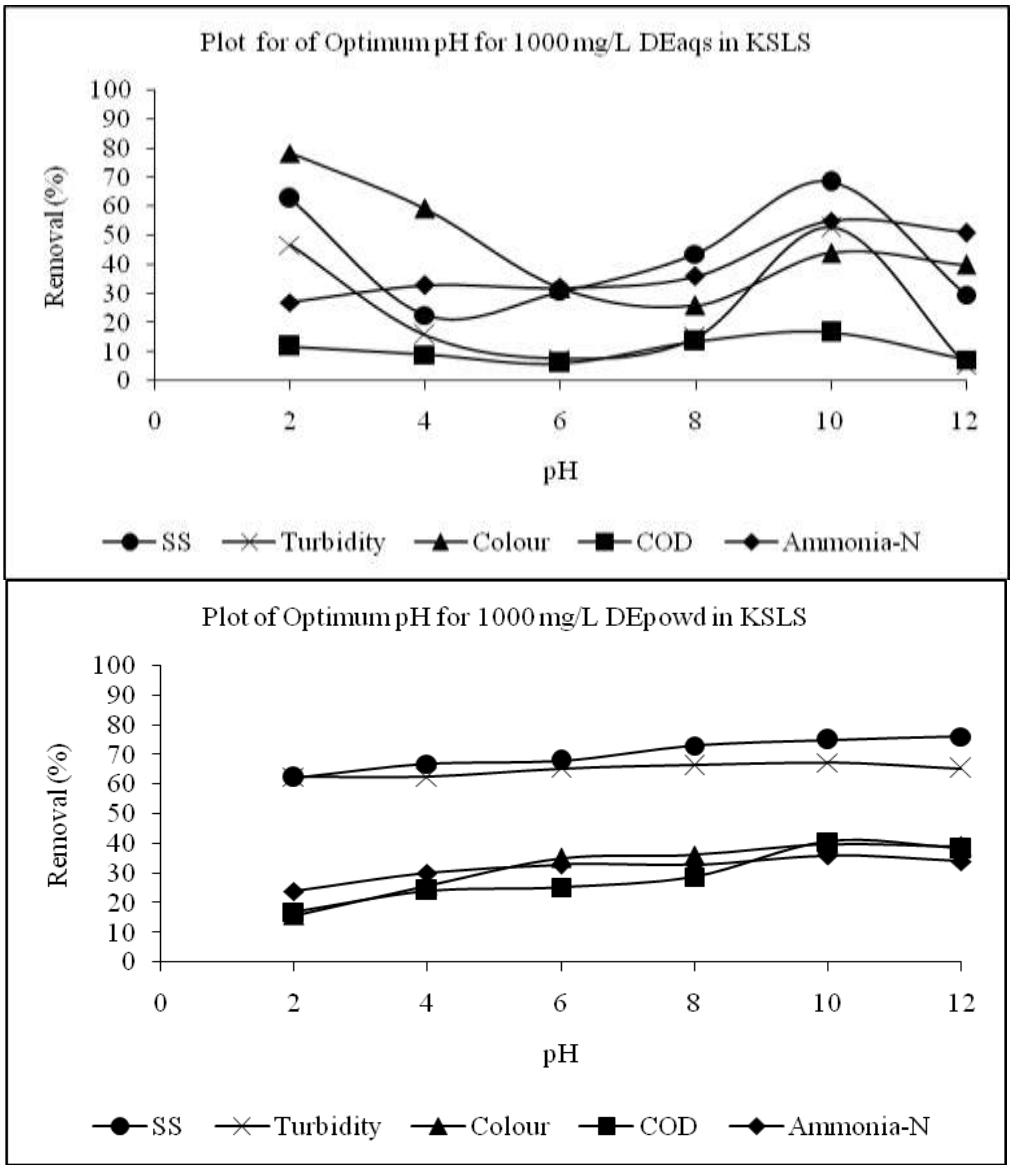

Figure 4.9: Percentage removal of SS, turbidity, colour, COD and ammonia-N vs pH of DEaqs and DEpowd in KSLS landfill leachate

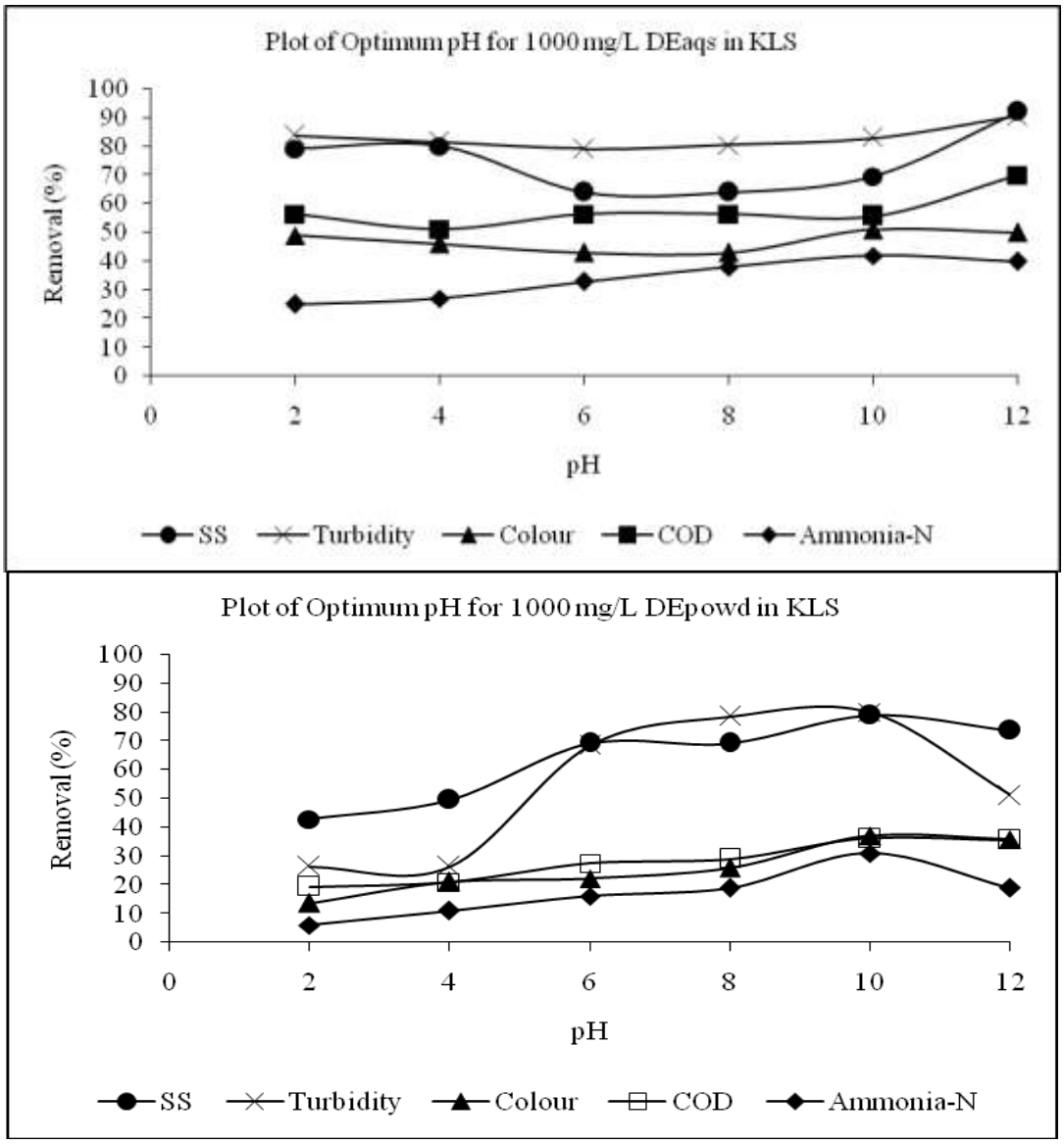

Figure 4.10: Percentage removal of SS, turbidity, colour, COD and ammonia-N vs pH of DEaqs and DEpowd in KLS landfill leachate

Figure 4.10 shows that the removal pattern of DEaqs for SS, turbidity, color, and COD in the KLS sample is different from that of the leachate samples treated by DEpowd. DEaqs demonstrated high removal rates at the peak pH values of 4 and 12. However, these two peak pH values were also found in other coagulation studies. Aziz et al. (2007b) found a similar curve in which the two peak pH values were 4 and 12, with ferric sulfate producing a lower color removal percentage at pH values of 6 and 7. Syafalni et al. (2012) reported that a better COD and colour removal could be achieved at a lower pH value (pH 2) by using lateritic soil as a coagulant. Figures 4.9 and 4.10 show a lower removal of the measured parameters at pH values of 6 and 7. This result, which can be attributed to the neutralization of the solution rather than of the acidic and basic pH, was also demonstrated in the aforesaid studies. The increased concentration of either H^+ or OH^- generates additional electrostatic forces between the coagulant and the chemical species in the landfill leachate, as well as promotes the coagulation process (Idris et al., 2013).

pH exhibited an obvious effect on the coagulation of the studied parameters in both KSLS and KLS by using DEaqs and DEpowd. This result was inconsistent with that of other researchers, such as Sanghi et al. (2006), Mishra et al. (2004), and Agarwal et al. (2001), who argued that natural polysaccharides or polymers are usually inert to pH changes. Therefore, the CA incited by the variations in pH results from the effect of pH on the constituents of the water samples. Given that pH plays an important role in metal hydroxide precipitation by changing the chemical entities of water or wastewater, the pH value must be adjusted to avoid such effect and to evaluate the removal of the measured parameters through the coagulation–

flocculation process, as previously reported by Beltràn-Heredia and Sànchez-Martin (2009).

Therefore, jar test experiments were performed at different dosages and pH values to prove that the studied parameters were solely removed via natural precipitation. DEaqs was tested at pH 6, 8, and 10 in the KSLS samples and at pH 4, 10, and 12 in the KLS samples. DEpowd was tested at pH 10 in both KSLS and KLS samples. Blank samples (without the addition of coagulants) were used to define CA by using pH. The removal percentage was higher at pH 4 and 12 despite the absence of coagulants, and almost remained constant at varying dosages of DEaqs in both KSLS and KLS samples (Figures 4.12 to 4.14) because of the influence of NaOH or H_2SO_4. Therefore, NaOH (alkaline) or H_2SO_4 (acid) can simultaneously serve as coagulants (Section 2.15) in addition to other factors, such as IEP and charged particles in the leachate sample.

The adsorption of DEaqs and DEpowd demonstrates several complex phenomena. As reported by Pefferkorn (1999), this situation is expected to become more complex when the suspending liquid medium contains components that can modify the polymer characteristics, such as complex ions and surfactants. Section 4.6.2 discusses this matter further by providing clear examples.

4.6 Optimum Dosage

After solving the issue of optimum pH, the optimum dosage for the coagulate must also be determined. The general experimental approach was to characterize the relationship of coagulant dosage and pH with the removal of SS, turbidity, color, COD, and NH_3-N using an optimized dosage of PACl, DEaqs, and DEpowd.

4.6.1 Effect of Coagulant Dosage for PACI

Coagulation dosage is one of the most important parameters that can determine the optimum condition for the performance of coagulants in the coagulation–flocculation process. Insufficient dosage or overdosing results in a poor flocculation performance. The effect of coagulant dosage on the removal of SS, turbidity, colour, COD, and NH_3-N in the KSLS (0 mg/L–5000 mg/L) and KLS (0 mg/L–1000 mg/L) samples is shown in Figure 4.11 (Appendix D (a) 1 and D (b) 2, respectively). The optimum pH value of the leachate samples from both sites were adjusted to 6 (Section 4.5.1) before coagulation. Optimum dosage in the KSLS and KLS samples was determined based on SS and turbidity removal because the coagulation–flocculation process primarily focused on these two parameters. Therefore, the maximum removals were observed at concentrations of 2000 and 500 mg/L in the KSLS and KLS samples, respectively.

Based on the results, the pollutant removal percentage increased as the coagulant dosage was increased up to the optimum level or beyond, which gradually decreased the RE (Makhtar et al., 2010; Park et al., 2008). The removal percentage of

NH_3-N remained constant and low (31%–38% in the KSLS sample, and 27%–31% in the KLS sample) at all coagulant dosages.

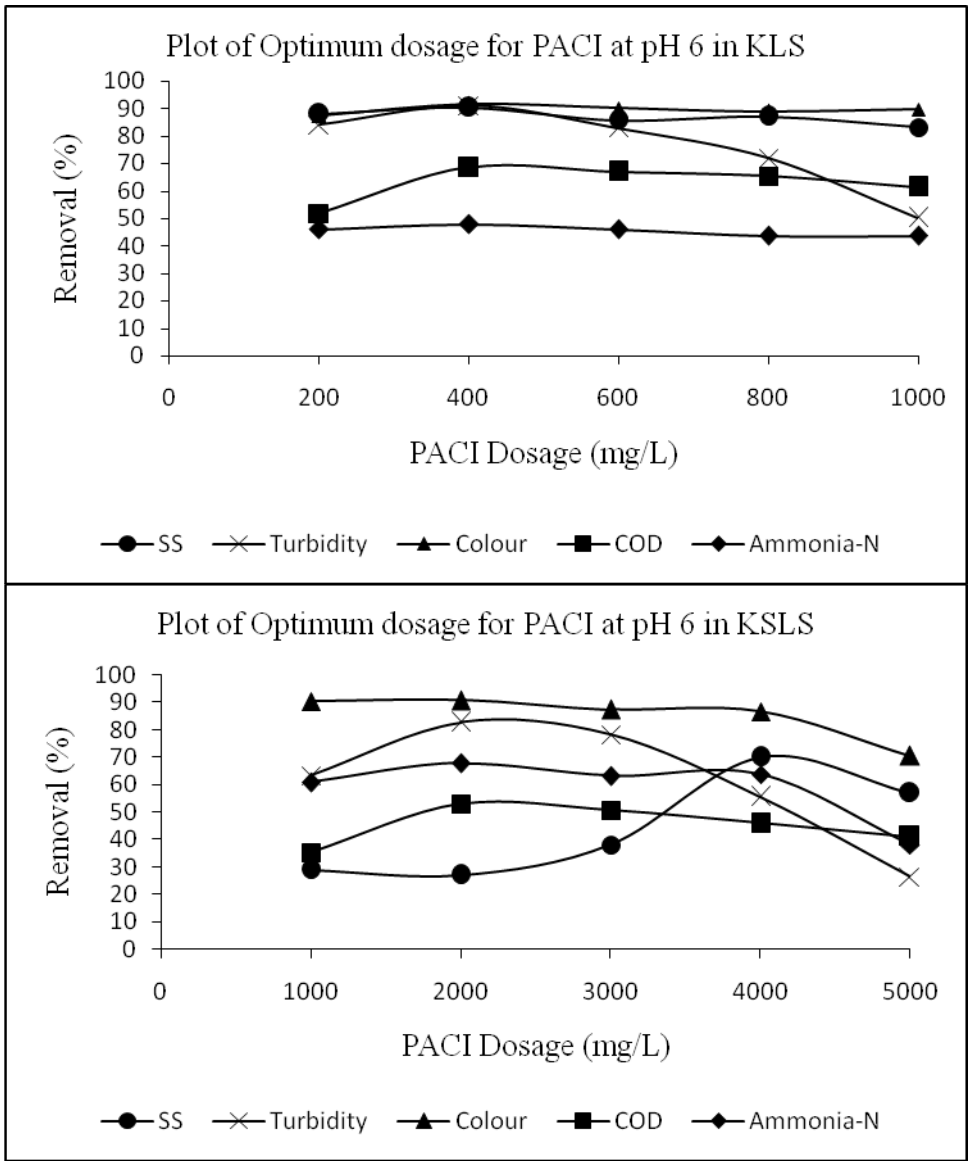

Figure 4.11: Percentage removal of SS, turbidity, colour, COD and ammonia-N vs dosage of PACI in KSLS and KLS leachate

PACl demonstrated an excellent peformance in removing colour compared with other parameters. The increase in colour RE is attributed to the increase in concentration of various hydrolysis species that destabilize the colloidal particles in landfill leachates. The addition of a larger dosage of coagulants reverses the surface charge of the particles because of the continued adsorption of monomeric and polymeric metal hydroxyl species of PACl. Bratby (2006) stated that an excessive coagulant dosage will result in the re-dispersion of colloidal particles, subsequently reducing colour RE.

4.6.2 Effect of Coagulant Dosage for DEaqs and DEpowd

Figure 4.12 to 4.14 (Appendix D (a) 2,3,4,5 and D (b) 2,3,4,5, respectively), represent the removal of SS, turbidity, colour, COD and ammonia-N from KSLS and KLS samples using DEaqs and DEpowd at various pH and coagulant dosages.

Overdose region (Section 2.15) was best explained by Figure 4.14, where DEpowd at pH 10 was employed to treat leachate samples in removing of colour and ammonia-N at KSLS and for KLS, the overdose region is described for the removal of turbidity and COD. Below 1000 mg/L (KSLS) and 200 mg/L (KLS), there was the underdose region where low reduction of measured parameters were illustrated. The removal rates slowly decreased beyond 1000 mg/L and 200 mg/L at KSLS and KLS, respectively as DEpowd dosage were increased.

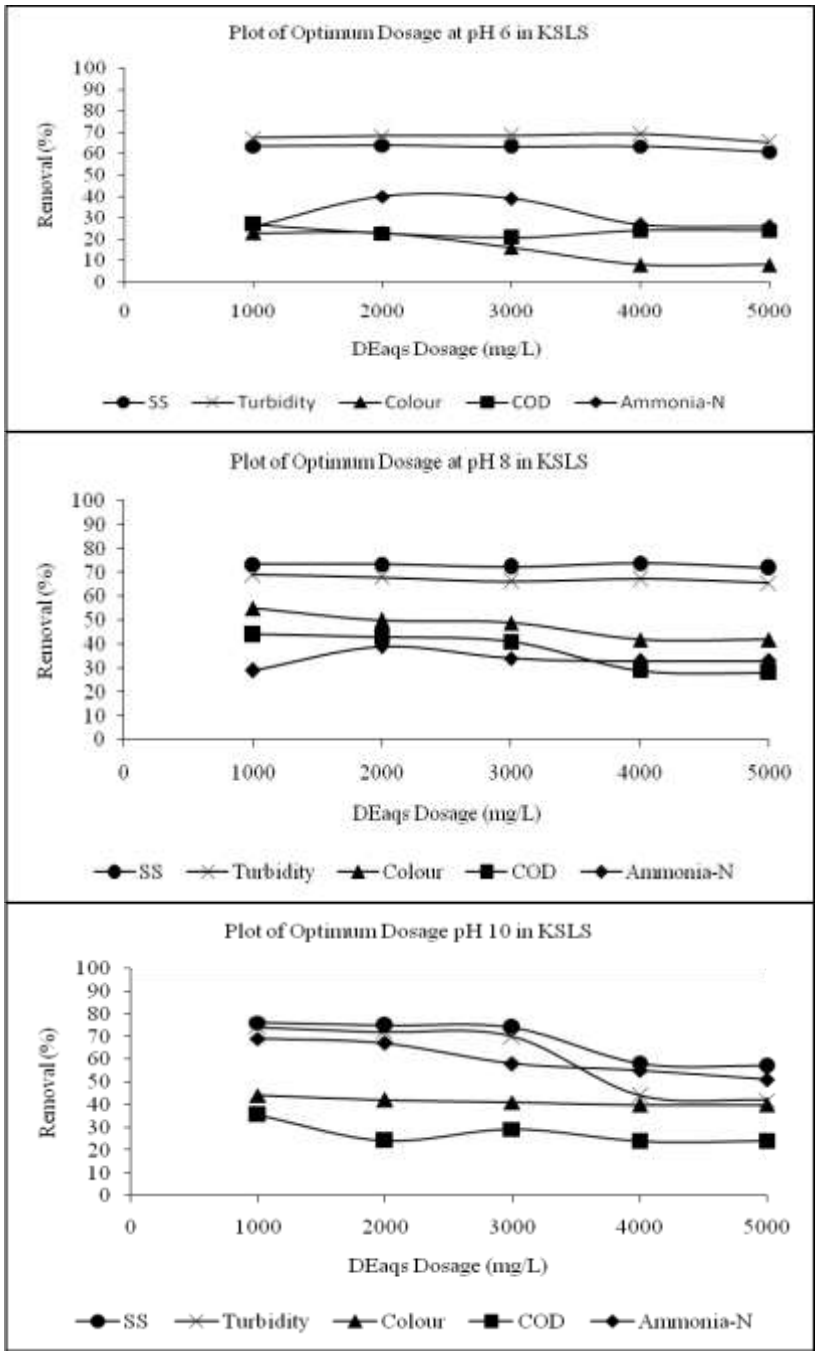

Figure 4.12: Effect of optimum dosage for DEaqs at KSLS

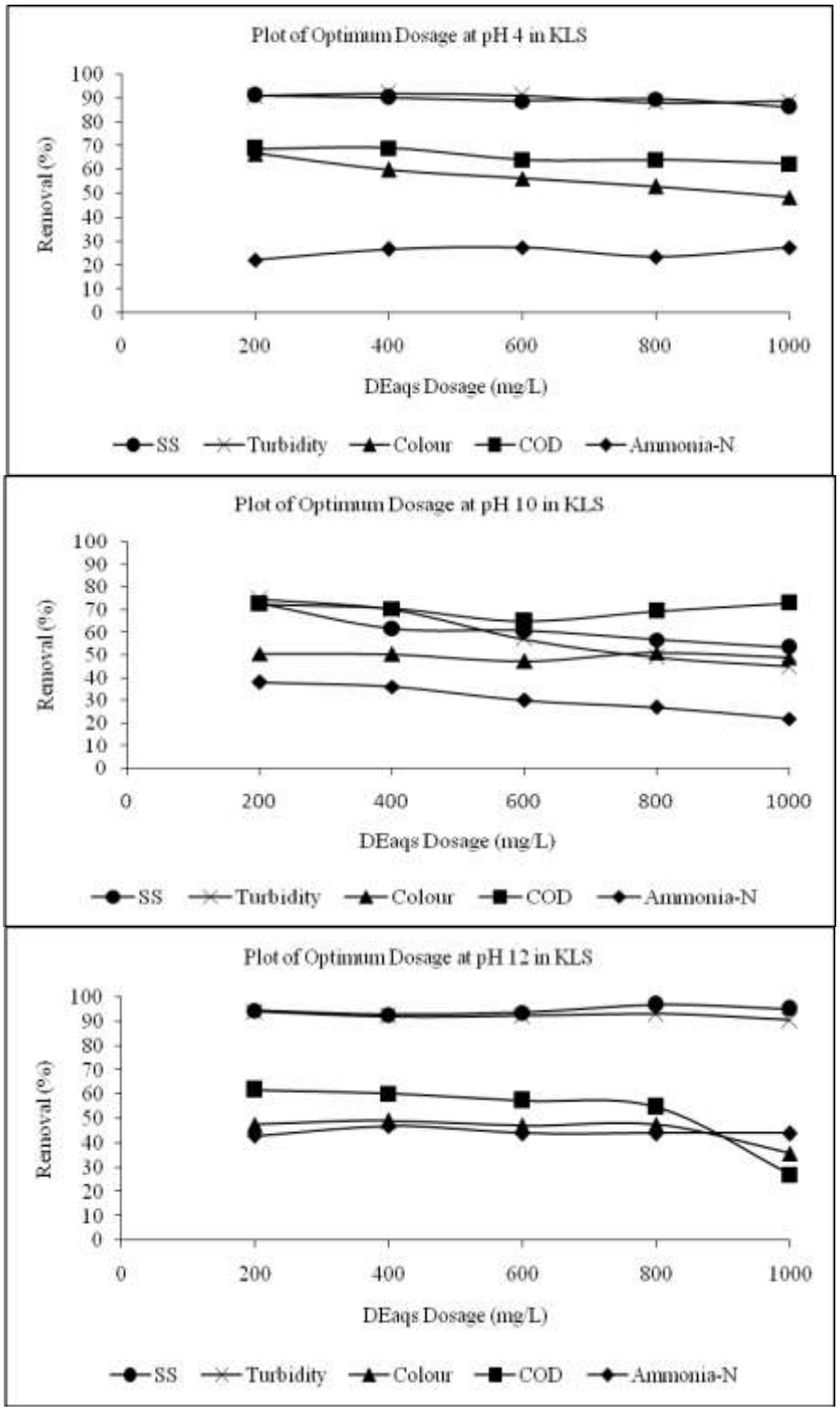

Figure 4.13: Effect of optimum dosage for DEaqs at KLS

As can be seen in Figure 4.13, there were also a removal pattern that showed an overdose of polymer do not alter the removal rates but indeed, increased the removal rates. For instance, removal rates for SS, turbidity and COD by DEaqs at pH 10 in KLS sample increased again after overdose region which is at 600 mg/L. Another example was removal rates for colour by DEaqs (pH 8) in KSLS (Figure 4.12).

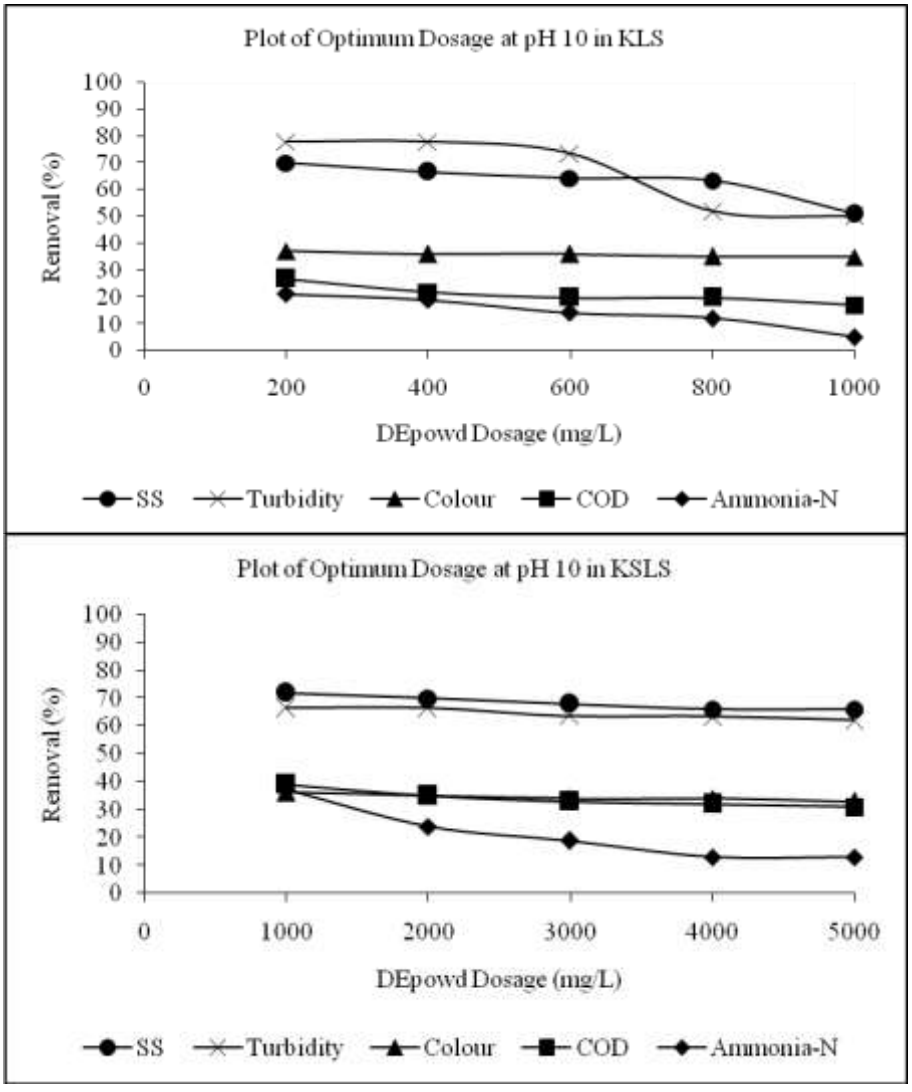

Figure 4.14: Effect of optimum dosage for DEpowd at KSLS and KLS

Based on the results in Figure 4.12 to 4.14, the removal performance was related to the pH of the solutions and the variations in pH dominated DEaqs and DEpowd performance. In general, under a given dosage of DEaqs and DEpowd, a lower removal rate was observed at intermediate pH 6 and 10 compared to pH 4 and 12. Hence, to justify an optimum pH and dosage for DEaqs and DEpowd was relatively difficult. Further analysis was carried out on each parameter which is discussed in Section 4.6.2.1 to Section 4.6.2.4. The results for the optimum dosage will be presented later (Section 4.6.2.5).

4.6.2.1 Turbidity and SS Removal

The relationship between turbidity and SS has been repeatedly and consistently identified (Daphne et al., 2011; Hannouche et al., 2011; Gippel, 1995). However, no universal relationship has ever been developed between turbidity and SS because they measure different objects and their values are functions of different variables. Turbidity reflects the loss of transparency in landfill leachates brought about by the presence of colloidal and/or SS. Turbidity is a direct function of the size, shape (Clifford et al., 1995; Gippel, 1988), colour (Malcolm, 1985), and reflectivity of the particles (Bhargava and Mariam, 1991). SS generally depends on the weight of the suspended particles and is a direct function of the number, size, and specific gravity of the particles. Figures 4.16 and 4.17 show a high correlation between turbidity and SS because the sampling was performed at a specific site. This finding was consistent with that of Pfannkuche and Schmidt (2003) and Lewis et al. (2002).

Figures 4.15 and 4.16 show that the turbidity and SS removal performance of PACl, DEaqs, and DEpowd were generally higher in the KLS sample than in the KSLS sample. As mentioned in Section 4.1, the individual particles in the KLS sample had greater size (691.4 d.nm) than those in the KSLS sample (346.5 d. nm). Given its large volume and weight, a larger particle provides a greater contribution to SS compared to a small particle; in contrast, a smaller particle provides a greater contribution to turbidity compared to a larger particle (Thackston and Palermo, 2000). The larger particles will settle out from the solution before the smaller particles under normal conditions. The dredging of fine particles, which usually overlay turbid waters, may explain why the turbidity and SS in the KLS sample can be removed more effectively than those in the KSLS sample.

The wasterwater colour (black or dark brown in the KSLS sample and light brown to yellow in the KLS sample) also generated variances in the efficiency of coagulants in the coagulation–flocculation process. The coloured dissolved organic matter is unlikely to alter the turbidity reading by 10% (Gippel, 1995). The intensity beam is primarily reduced by the SS through light scattering. However, the absorption (colour) from the dissolved substances can also reduce the light intensity. As a result, the detector senses a less-scattered light, providing a false and lower-than-actual turbidity reading (Omega.Com, 2010).

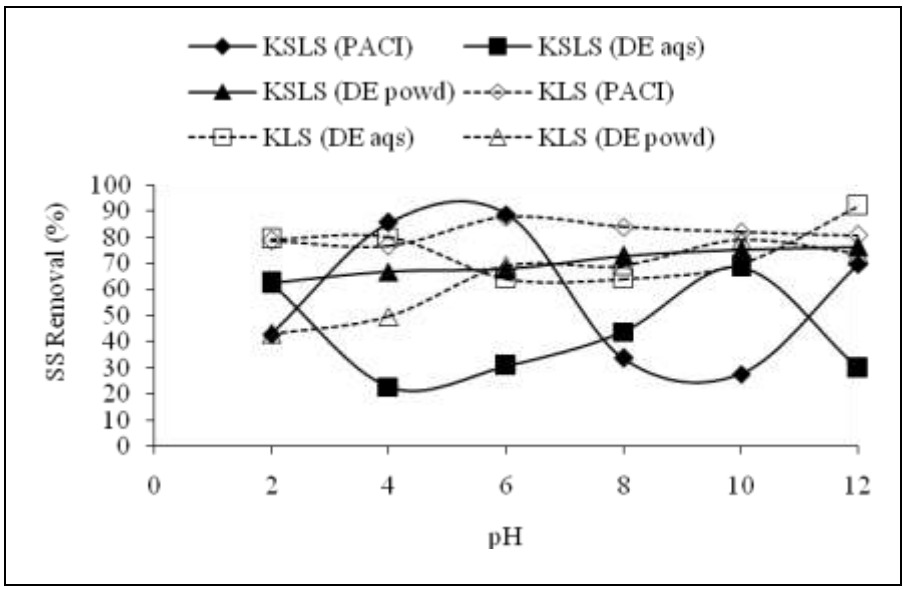

Figure 4.15: SS removal by PACI, DEaqs and DEpowd as a function of pH in KSLS and KLS leachate

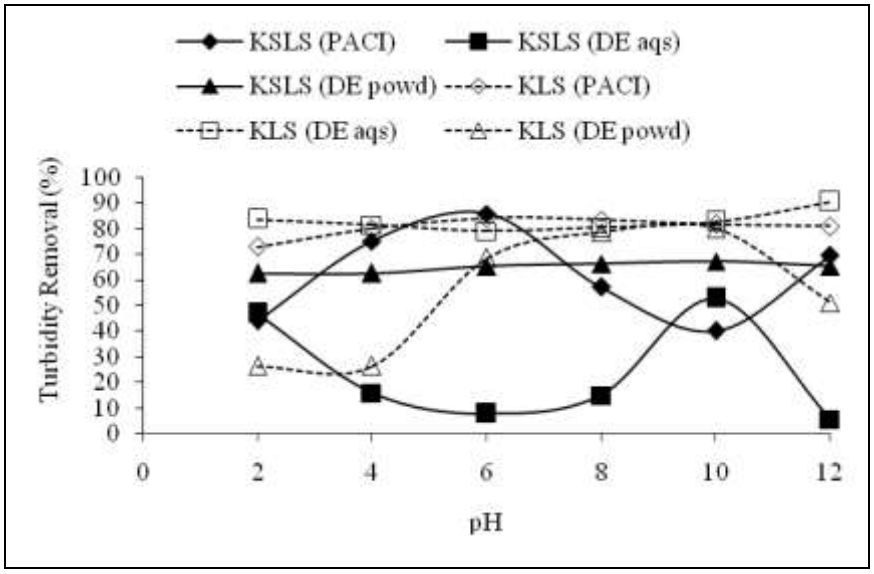

Figure 4.16: Turbidity removal by PACI, DEaqs and DEpowd as a function of pH in KSLS and KLS leachate

Figures 4.15 and 4.16 show that pH 10 contributes to the favorable performance of DEaqs and DEpowd in the coagulation–flocculation process. However, a low (pH 2 to 4) and high pH (pH 12) indicate higher supernatant turbidity and SS values from the KLS leachate samples. These results are in accordance with the observation that higher pH values are optimal for other natural coagulants, such as natural stone powder (Basaran and Tasdemir, 2014), chestnut and acorn (Ŝćiban et al., 2009), *C. opuntia* (Zhang et al., 2006), *M. oleifera* (Okuda et al., 2001a and 2001b), and *P. juliflora* and *Cactus latifaria* (Diaz et al., 1999).

In the coagulation–flocculation process, the potential of the particle surface affects the stabilization or destabilization of the suspended particles as well as the efficiency of the process. The stability of the particles is determined by analyzing the typical zeta potential versus plot. When the magnitude of the zeta potential is high, the electrostatic repulsion between particles causes the particles to disperse readily, whereas the electrostatic repulsion between particles causes the particles to disperse and form stable suspensions.

When the magnitude of the zeta potential is low, the repulsive force between the particles is reduced to attract the particles closer to one another and form agglomerates, which results in faster settling characteristics. The particles are assumed to fall in a stable region when their zeta potential values exceed ± 30 mV (Yarar, 2001). The plot of zeta potential versus pH in Figure 4.1 (Section 4.3.1) shows that the zeta potential values of DEaqs varies between +2.66 and –4.17 for a pH range of 2 to 4 and settles at +1.24 for a pH value of 12. Particles in the suspensions are assumed to fall in the unstable region. The increased concentration

of either H^+ or OH^- produces more electrostatic forces between the coagulant and the chemical species in the landfill leachate as well as enhances the flocculation of particles. This phenomenon explains the favorable response of DEaqs in the KLS leachates toward the process outlined in Figures 4.15 and 4.16.

The curve trend for turbidity, which shows low CA, falls under a pH range of 5 to 8 for DEaqs and DEpowd in both KSLS and KLS samples. This result was similar to that obtained by Ŝćiban et al. (2009), who observed a low CA for turbidity removal by chestnut and acorn in a pH range of 5 to 8. Based on Figures 4.17 and 4.18, DEaqs managed to suppress PACl in removing more than 80% of SS and turbidity over the dosage range tested at a specific pH value. Figures 4.17 and 4.18 show that a 200 mg/L dose of DEaqs at pH 12 can sufficiently remove a high amount of SS and turbidity, though the same removal rates of the measured parameters are also observed at a dosage of 800 mg/L.

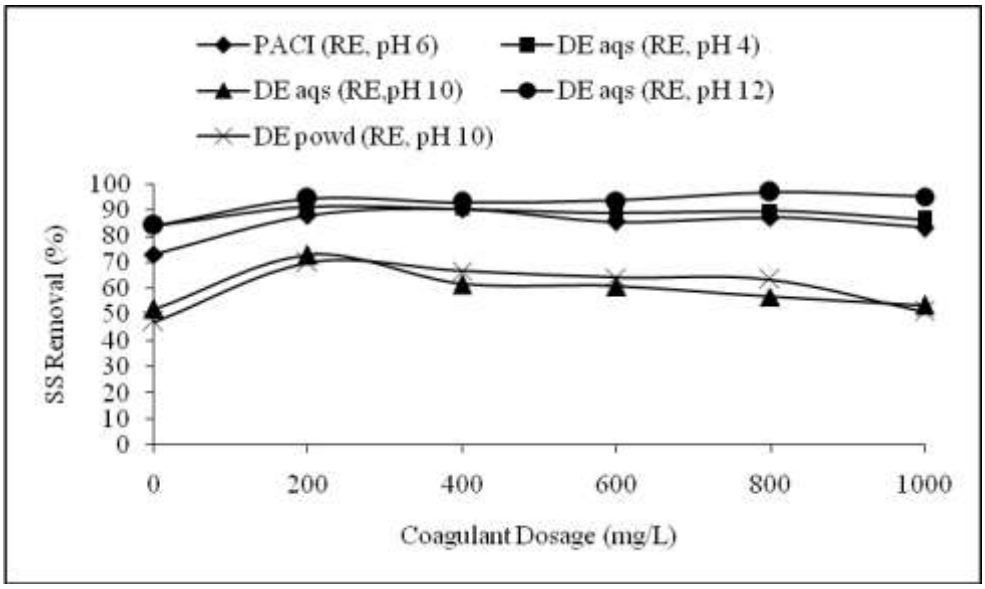

Figure 4.17: Effect of coagulant dosage and pH on SS removal of PACI, DEaqs and DEpowd in KLS leachates

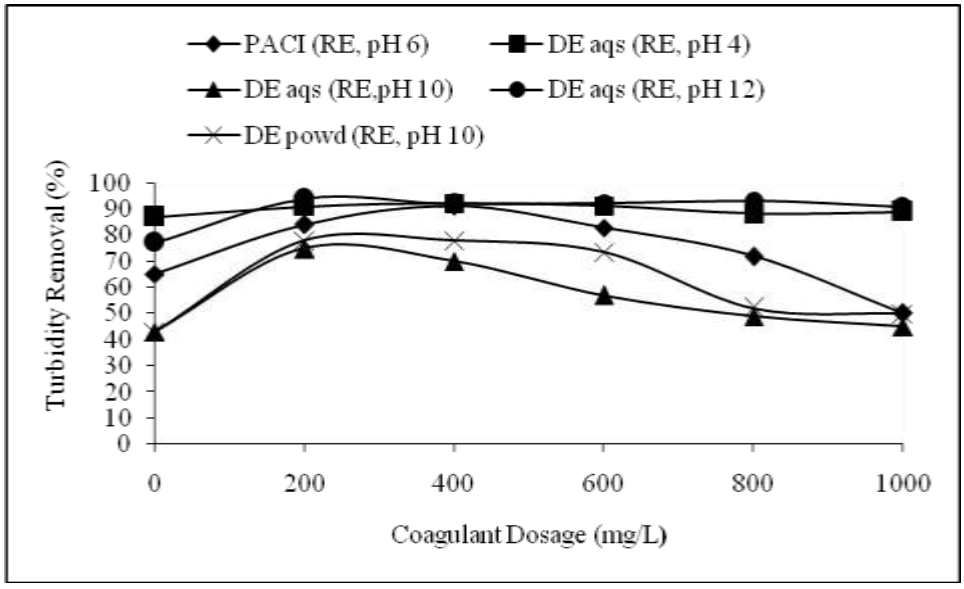

Figure 4.18: Effect of coagulant dosage and pH on turbidity removal of PACI, DEaqs and DEpowd in KLS leachates

To prove that this high efficiency was solely produced by DEaqs, a CA plot is illustrated in Figures 4.19 and 4.20, which show a positive result. An increase in pH value has a positive effect on the coagulation activities of DEaqs in removing SS and turbidity from the KLS sample. DEaqs can suppress PACl and serve as a coagulant at different pH values. The CA for PACl in removing SS from the KLS sample was 0.65, whereas the CA for DEaqs was 0.4 and 0.55 at pH 4 and 12 respectively. The CA for PACl in removing turbidity from the KLS sample was 0.75, whereas the CA for DEaqs was 0.39 and 0.75 at pH 4 and 12 respectively.

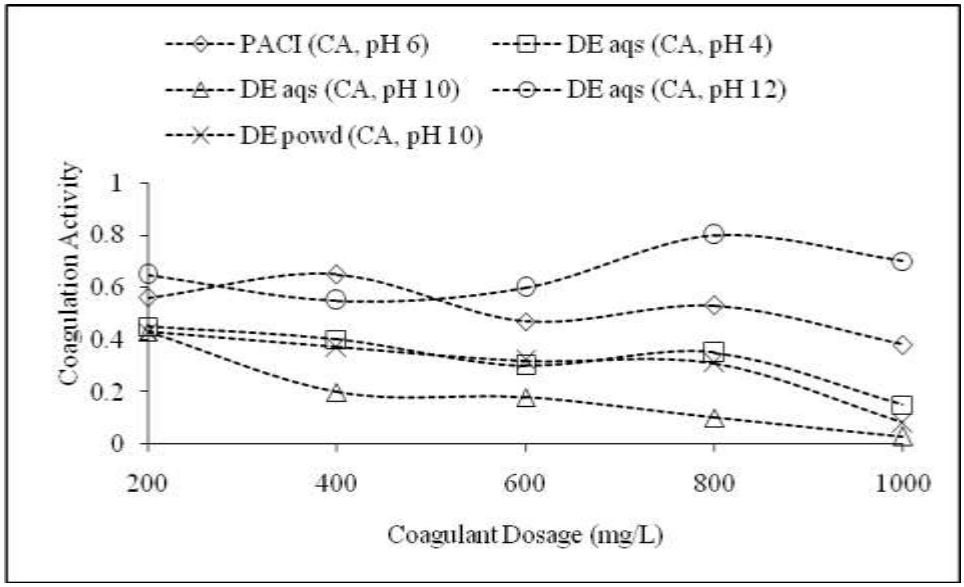

Figure 4.19: Effect of coagulant dosage and pH on coagulation activity of PACI, DEaqs and DEpowd based on SS removal in KLS leachates

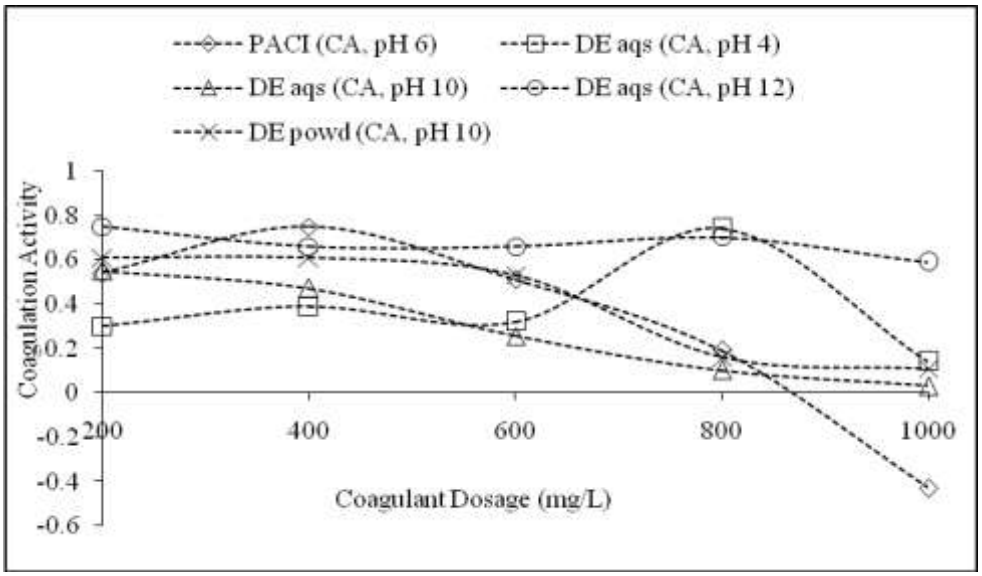

Figure 4.20: Effect of coagulant dosage and pH on coagulation activity of PACI, DEaqs and DEpowd based on turbidity removal in KLS leachates

Exceeding the optimum coagulant dosage of PACl, DEaqs, and DEpowd (> 2000 mg/L) significantly decreased the SS and turbidity RE of these coagulants in the KSLS sample (Figures 4.21 and 4.22). This fluctuating trend was also reported by Anastasakis et al. (2009), who found that the optimum amount of coagulants in the suspension aggregated and settled the maximum amount of particles. Exceeding the optimum dosage also leads to the steric stabilization of the particles, which subsequently increases the concentrations of SS and turbidity. The RE of PACl decreased as the dosage was increased, which suggested that charge neutralization improved the removal of particles in the KLS and KSLS samples. The proposed dosage for DEaqs and DEpowd in the KSLS sample was 1000 mg/L while the proposed dosage for DEaqs and DEpowd in the KLS sample was 200 mg/L.

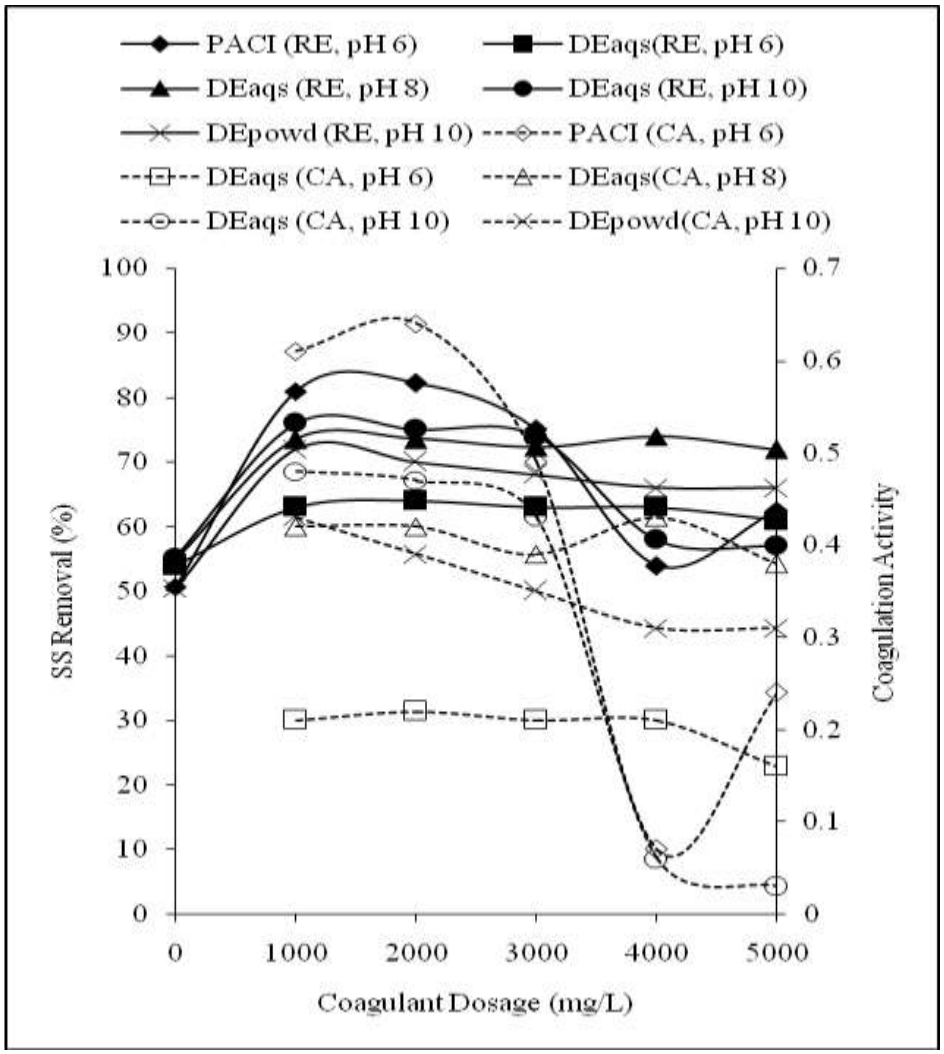

Figure 4.21: Effect of coagulant dosage and pH on SS removal and coagulation activity of PACI, DEaqs and DEpowd in KSLS leachates

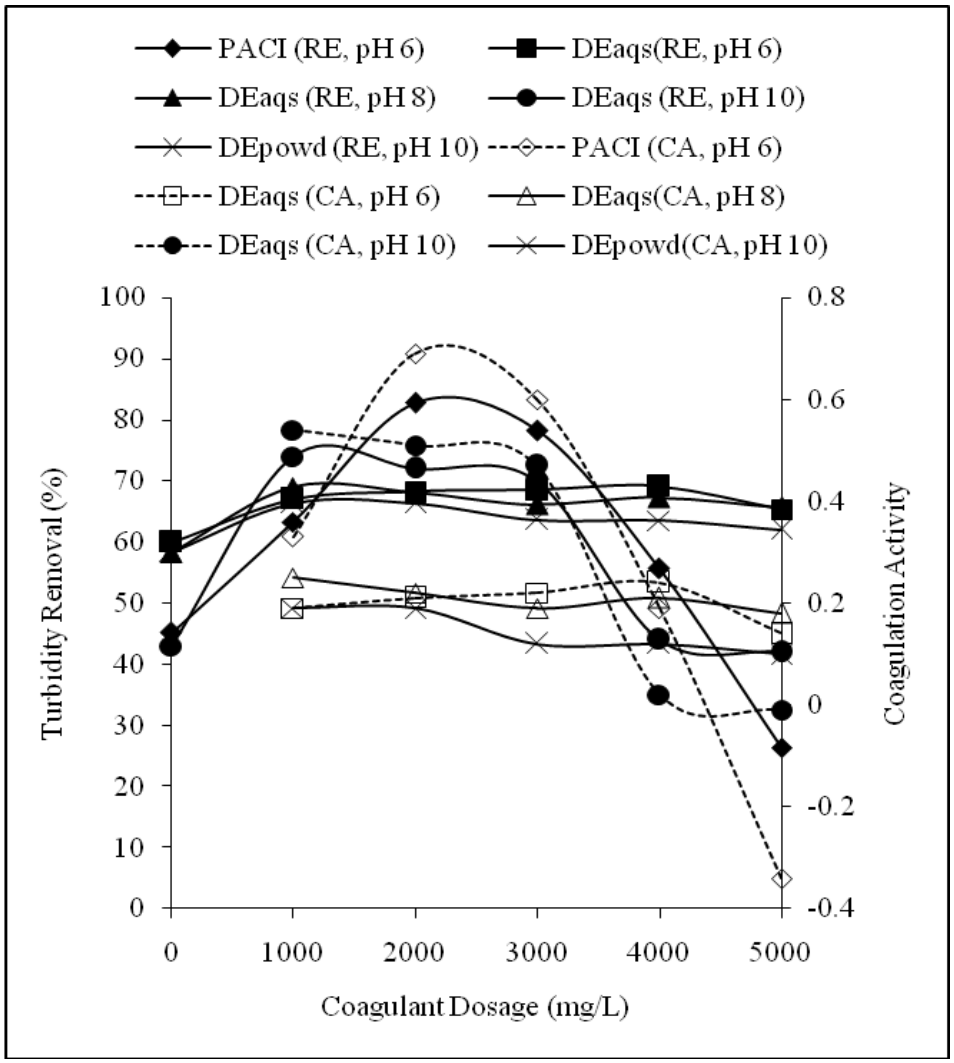

Figure 4.22: Effect of coagulant dosage and pH on turbidity removal and coagulation activity of PACI, DEaqs and DEpowd in KSLS leachates

4.6.2.2 Colour Removal

Figure 4.23 shows that the optimum pH for achieving colour RE is either at low (pH 2) or high pH (pH 12) because the dissolution of metal ions increases at lower pH values, which incites competition between the electrolyte cations and the metals adsorbed to the colloidal particles by increasing the positive charge of the coagulant solution (Lombnaes et al., 2008). Consequently, the negatively charged

particles in the landfill leachate are further reduced or neutralized to enhance coagulation performance.

An increase in pH also deprotonated the functional hydroxyl groups in the humic acids, DEaqs, and DEpowd, which produced high negative charges that were ready to be adsorbed onto or bridged with the divalent metal cations (i.e., Ca^{2+} and Mg^{2+}) in leachate solutions. At high pH, the solubility of the humic substances increased, whereas the surface charge of DEaqs and DEpowd decreased, which would lead to the coagulation process. Cheng (2002) stated that the hydrolysis rate of Al^{3+} ions was also enhanced at a high pH to form coagulation species with a low positive charge; hence, a higher coagulant dosage should be consumed to neutralize the surface charge (Cheng et al., 2004).

Figure 4.23 shows that the colour removal in a narrow pH range is lower than that in a wider pH range of PACl. The RE decreased from 78% to 59% and from 49% to 46% for DEaqs at KSLS. These results could be attributed to the organic materials and mineral surfaces that repel each other and limit the surface complex formation, which would subsequently release the organic materials into the DEaqs and DEpowd solutions as well as decrease the removal of colour from the leachate samples.

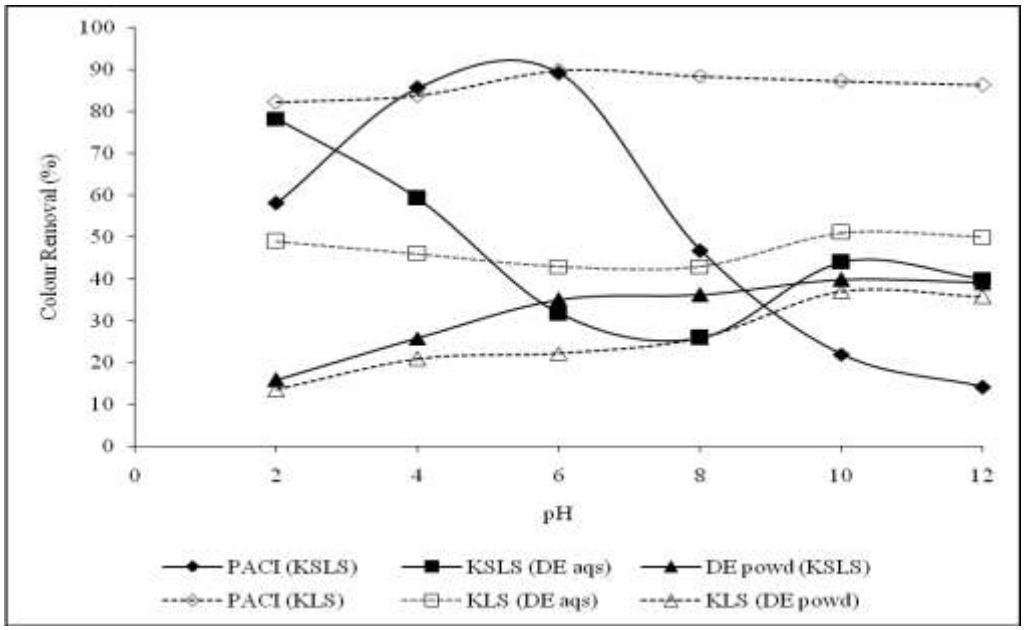

Figure 4.23: Effect of pH on colour removal by using 1000 mg/L PACI, 1000mg/L DEaqs and 1000 mg/L DEpowd at KSLS and KLS

Although an optimum colour removal could be achieved at pH 2, the coagulation experiments at different pH values were performed based on the cumulative results obtained from the removal of other measured parameters in this study. Given that the removal of SS and turbidity is prioritized in the coagulation–flocculation process, a low colour removal rate is expected. As shown in Figures 4.24 and 4.25, although DEaqs and DEpowd could still produce complexes with humic acids, the residual negative charges on these complexes prevent the flocculation and precipitation of these complexes. This finding echoes that of Cheng (2002) and Cheng and Chi (2002).

Therefore, the colour RE of DEaqs and DEpowd at pH 10 was low. In contrast, although the colour RE of DEaqs was high at a low pH (pH 4) (Figure

4.32), its CA in the KLS sample (pH 4) was very low compared to its activity in pH 10 and 12. Therefore, the color RE was affected by acid and not solely by DEaqs.

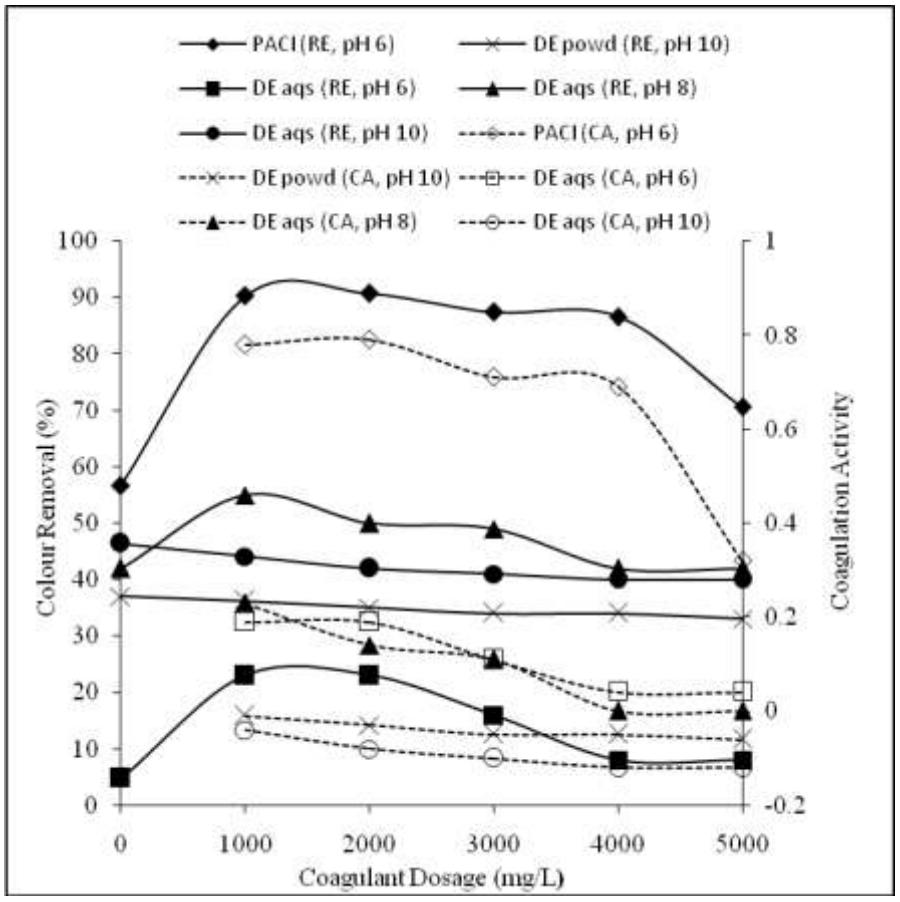

Figure 4.24: Effect of pH on colour removal at various PACI, DEaqs and DEpowd concentration in KSLS leachate sample

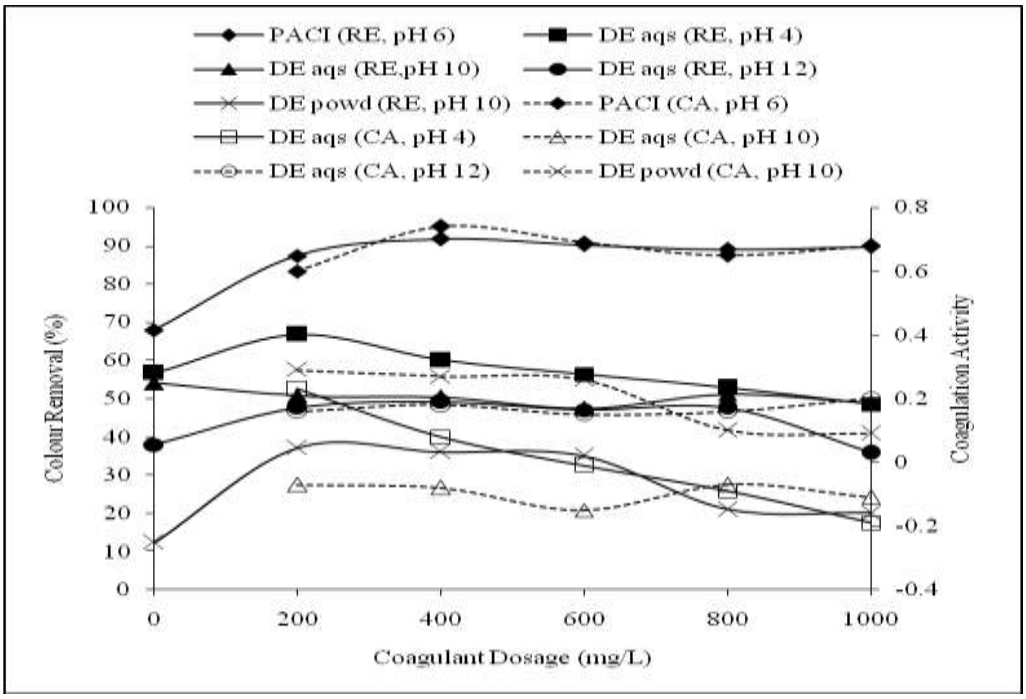

Figure 4.25: Effect of pH on colour removal at various PACl, DEaqs and DEpowd concentration in KLS leachate samples

By comparing the results of all coagulation experiments, PACl outperforms DEaqs and DEpowd in removing colour from the KSLS and KLS samples (Figures 4.24 and 4.25). The colour RE in the KSLS and KLS samples was considerably low in most dosage ranges when DEaqs and DEpowd were present as they increase the color concentration in the coagulated system. This observation is attributed to the inefficiency of DEaqs and DEpowd to induce a polymer bridging mechanism because of their coiled position in the leachate suspension. Therefore, attaching the polymer chain to the surface may become difficult and may adversely affect the flocculation. Many studies reported that the activity of polymers is related to their uncoiling or extension (Bolto and Gregory, 2007; Sabah and Erkan, 2006; Besra et al., 2004; Taylor et al., 2002; Somasundaran and Krishnakumar, 1997). For PACl,

increasing the coagulant dosage in the KSLS sample turned the raw leachate into dark brown, clear brown after sludge separation, yellow, and then clear yellow after using the optimum coagulant dosage and pH.

4.6.2.3 COD Removal

As can be seen in Figure 4.26, the influence of pH value on COD RE was examined using PACl, DEaqs, and DEpowd. The REs of PACl, DEaqs, and DEpowd were generally higher in the KLS sample than in the KSLS sample. A high COD removal rate could be achieved in the KLS sample by using DEaqs at a high pH and using PACl at an intermediate pH.

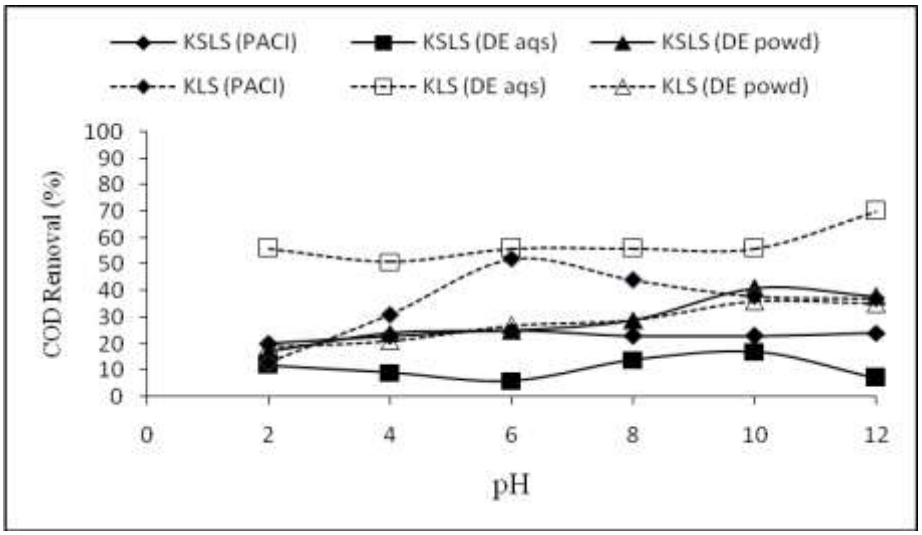

Figure 4.26: Effect of pH on COD removal at various PACI, DEaqs and DEpowd concentration in KLS leachate samples

As shown in Figures 4.26 to 4.28, the best COD removal rate and the highest CA were observed in the KLS sample. All coagulants demonstrated low removal rates below 50% in the KSLS sample because of the interaction of sulfide and iron (II) with the high content of inorganic matter in the leachates (Kylefors et al., 2003).

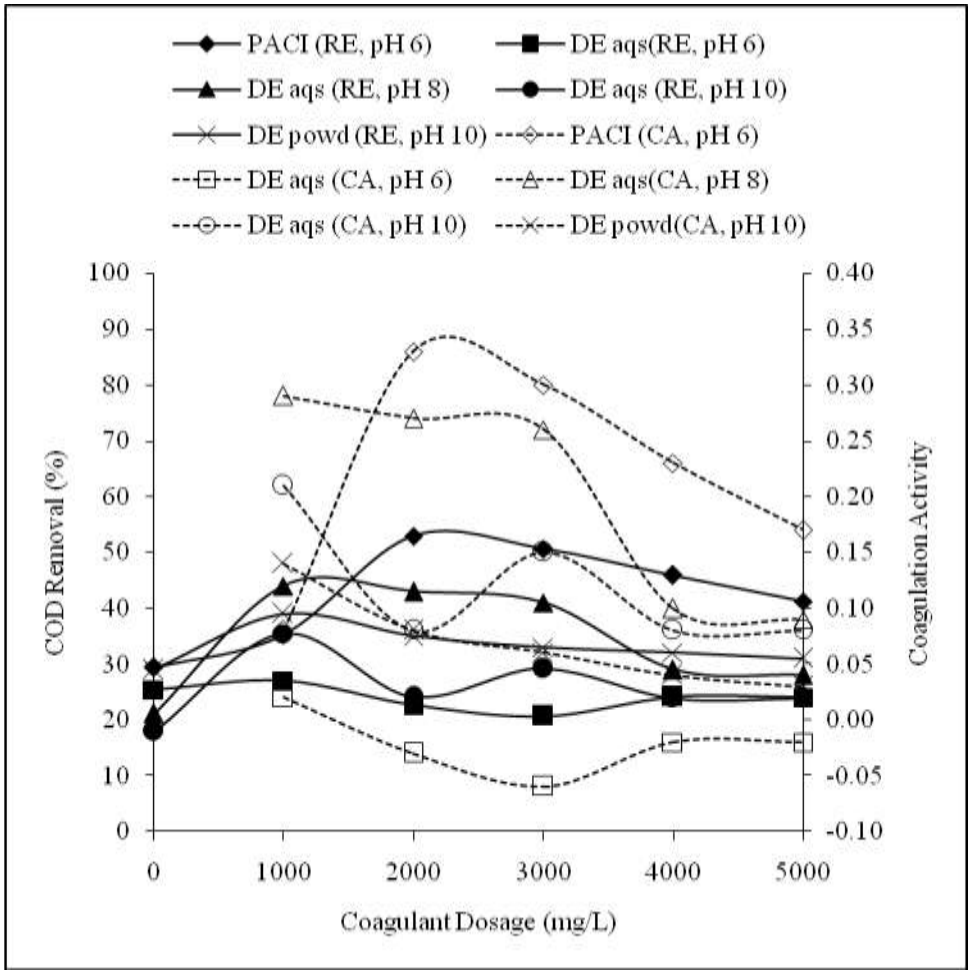

Figure 4.27: Effect of pH on COD removal at various PACI, DEaqs and DEpowd concentration in KSLS leachate sample

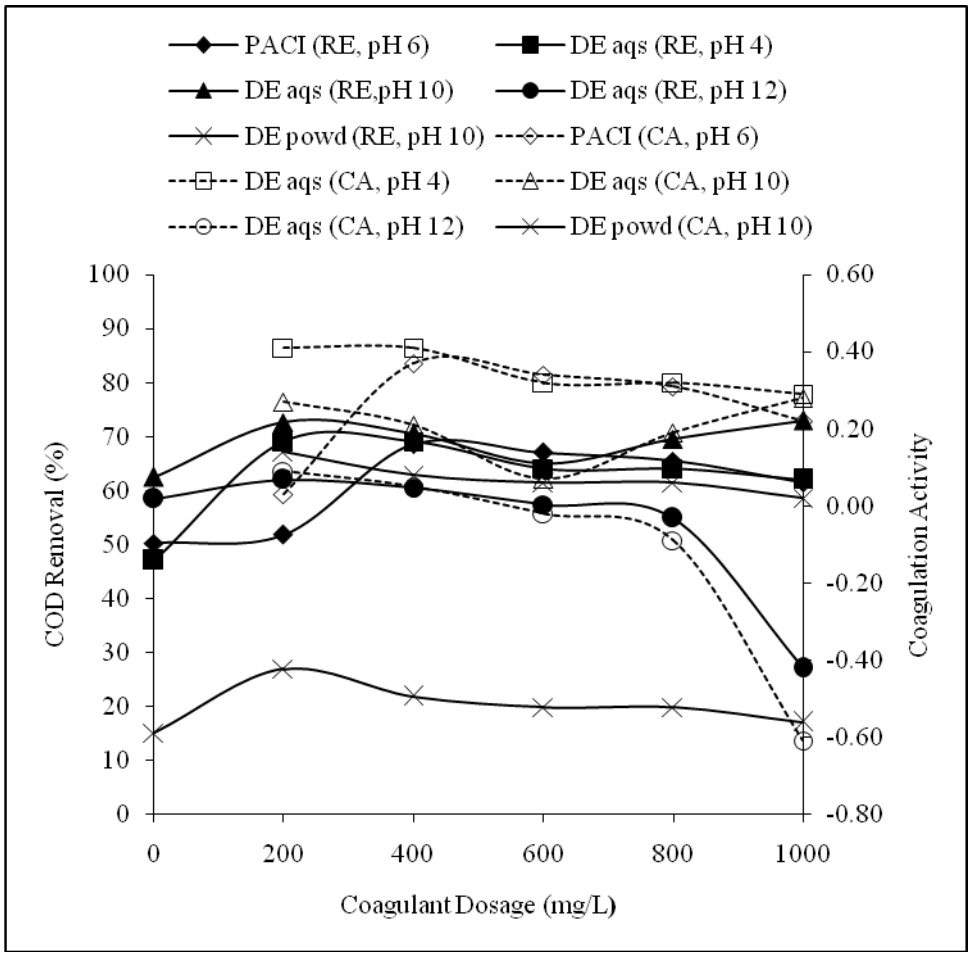

Figure 4.28: Effect of pH on COD removal at various PACI, DEaqs and DEpowd concentration in KLS leachate sample

Figures 4.27 and 4.28 show the effects of various dosages of PACl, DEaqs, and DEpowd on COD removal. The COD removal rate in the KLS sample gradually increased until an optimum dosage (200 mg/L for DEaqs and DEpowd, 400 mg/L for PACl) was reached, which could be attributed to the restabilization of colloidal particulates when the coagulant dosage exceeds the optimum value (Aziz et al., 2007b). These results were consistent with those of Zazouli and Yousefi (2008), who argued that the high COD removal rates were primarily caused by the fact that using

an optimum coagulant dosage produced flocs with a favorable structure and consistency.

Unlike DEaqs and DEpowd, increasing the dosage of PACl positively affected the removal of COD from KSLS leachates (Figure 4.28). Figure 4.28 shows that the removal of COD by DEaqs and DEpowd at pH 10 was linearly constant with increasing dosage, in which the difference in removal was approximately 0% to 10 %. Therefore, the proposed DEaqs and DEpowd dosage in the KSLS sample was 1000 mg/L.

4.6.2.4 NH_3-N Removal

Although several studies have investigated the removal of NH_3-N in wastewater, these reports have mostly focused on the adsorption process. This section briefly explains the experimental and adsorption results obtained in previous literature.

Landfill operators consider the presence of high concentrations of NH_3-N in landfill leachates as one of their main problems. The NH_3-N concentration in leachates may last for several decades; such high concentration resulted from the slow leaching process and the release of soluble nitrogen from solid waste in landfills (Aziz et al., 2004). Figure 4.29 shows that the NH_3-N RE slightly increased as the pH increased when DEaqs and DEpowd were used as coagulants. In a pH range of 9 to 10, the NH_3-N RE of DEaqs and DEpowd bested that of PACl by over 30%. At pH 10, DEaqs removed 55% and 42% of the NH_3-N in the KLS and KLS samples , DEpowd removed 36% and 31%, and PACl removed 29% and 24%. A higher

percentage of removed NH_3-N was achieved by using DEaqs and DEpowd at a high pH and by using PACl at an intermediate pH. Zheng et al. (2009) reported the potential of the chitosan-g-poly(acrylic acid)/attapulgite (CTS-g-PAA/APT) composite for removing NH_3-N from synthetic wastewater and found an obvious increase in NH_3-N removal beyond pH 8. The adsorption pattern of NH_3-N on CTS-g-PAA/APT with pH was similar to the results illustrated in Figure 4.36.

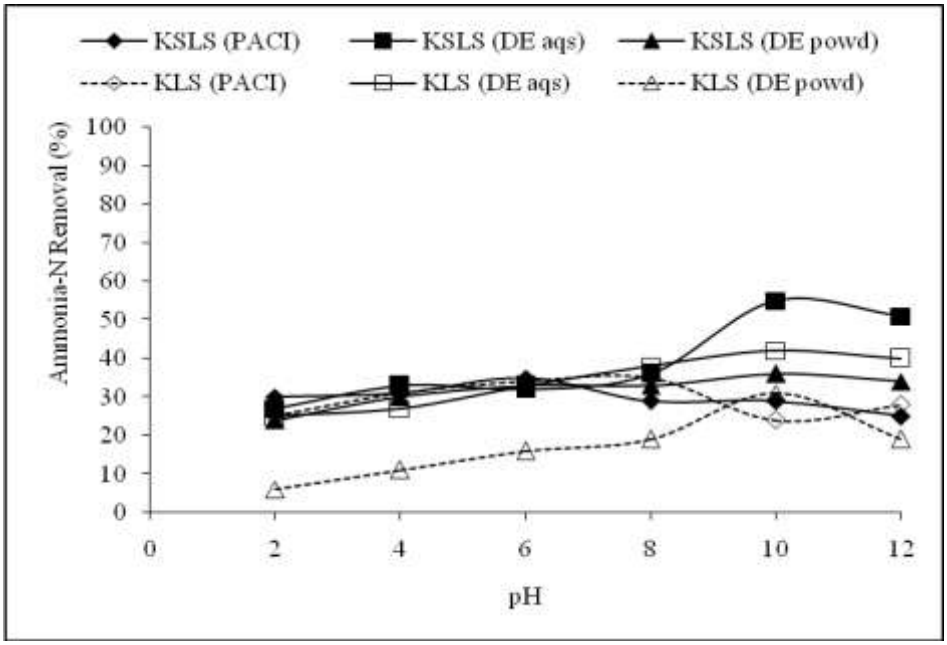

Figure 4.29: Effect of pH on ammonia-N removal by using 1000 mg/L PACI, 1000mg/L DEaqs and 1000 mg/L DEpowd at KSLS and KLS

According to Zheng et al. (2009), –C=O groups can be easily ionized and the ionization degree increased with increasing pH values because of the low pKa of PAA, which was 4.7. By using limestone and granular-activated carbon in batch studies, Hussain et al. (2006) reported that a pH value of 13 can effectively remove

41% of NH_3-N from synthetic wastewater. Figures 4.30 and 4.31 show that the NH_3-N RE of DEaqs is higher in the KSLS sample than in the KLS sample. At pH 10 and a dosage of 1000 mg/L, DEaqs demonstrated the highest NH_3-N removal (69%) in the KSLS sample compared to PACl and DEpowd. The possible removal mechanism for NH_3-N may be driven by the ion exchange potential for the charged pollutant, especially for materials with negative surface charges (Vimonses et al., 2009). As a positively charged species, ammonia-N acts as a bridging element between the anionic sites of the polymer chain (DEaqs) and the negative particles surface of landfill leachates, which are responsible for the coagulation process.

As shown in Figure 4.30, the positive CA of DEaqs in the KSLS sample indicated that the removal of NH_3-N was not solely dependent on chemical precipitation. Therefore, DEaqs could act as a coagulant and suppress PACl at different pH values. The CA in KLS was also low (Figure 4.31). An excess DEaqs dosage of 400 mg/L at pH 4 would result in sweep coagulation, whereas restabilization occurs in the DEaqs and DEpowd coagulants (pH 10 and pH 12). Therefore, the proposed dosage of DEaqs in the KSLS and KLS samples was 1000 and 400 mg/L respectively.

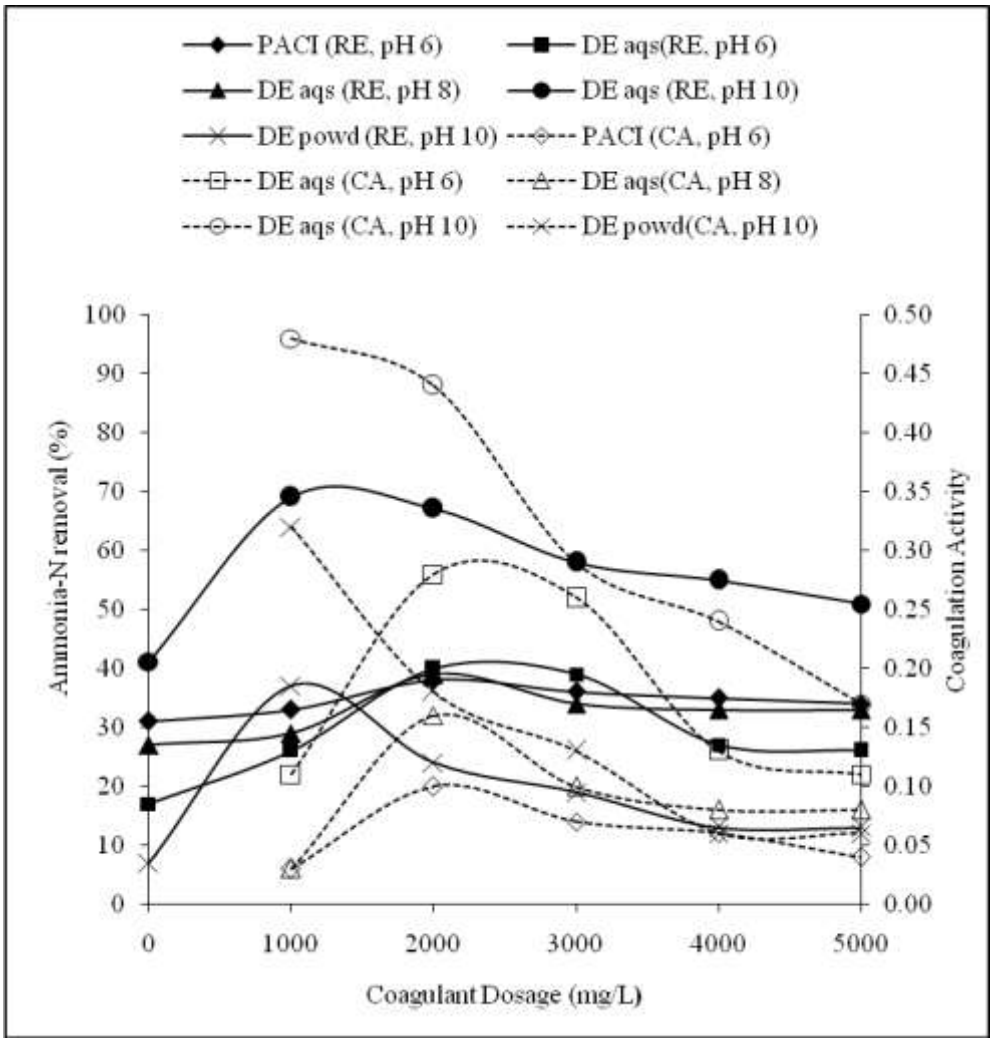

Figure 4.30: Effect of pH on ammonia-N removal at various PACI, DEaqs and DEpowd concentration in KSLS leachate

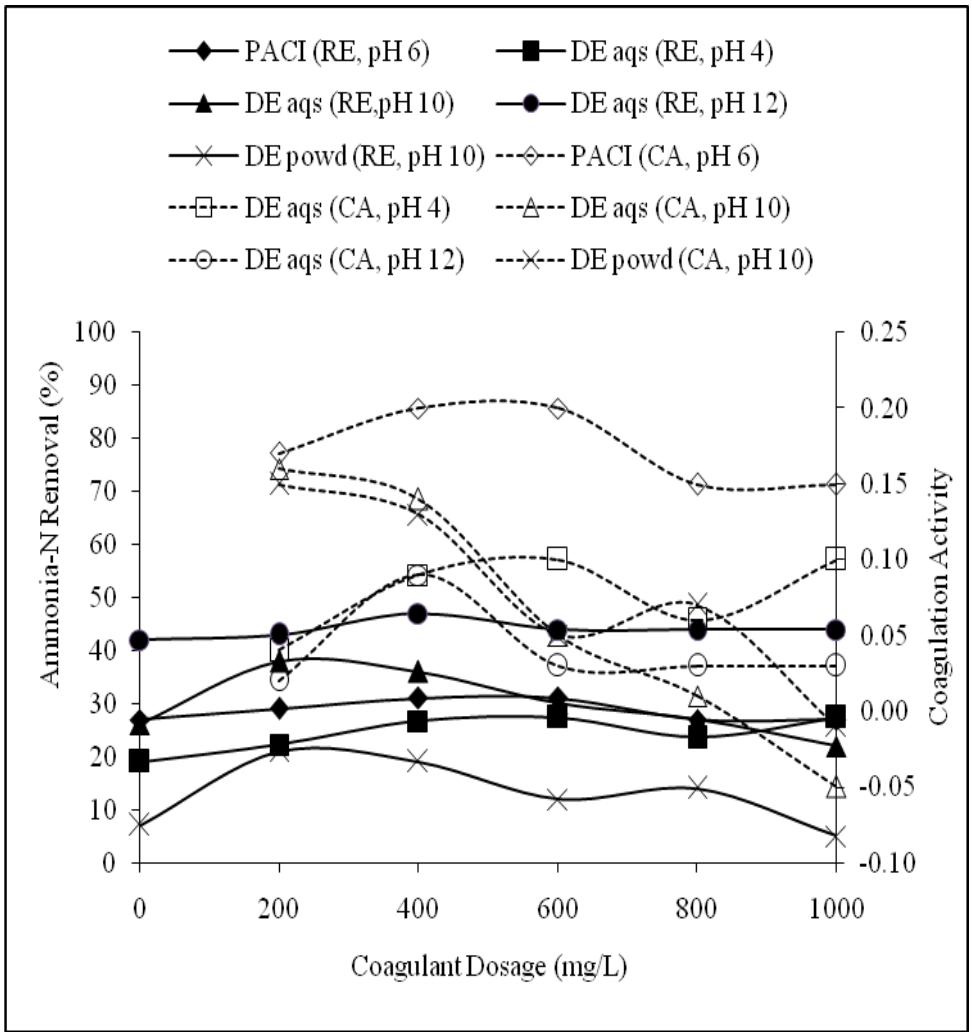

Figure 4.31: Effect of pH on ammonia-N removal at various PACI, DEaqs and DEpowd concentration in KLS leachates

4.6.2.5 Conclusion on Optimum DEaqs and DEpowd Dosage

Tables 4.7 and 4.8 present the highest RE of all measured parameters at optimum conditions. As can be observed from the results in Sections 4.6.2.1 to 4.6.2.4, it can be concluded that lower dosages of investigated natural coagulants were better than higher ones. These dosages are considered low compared to the optimum PACl dosages of 2000 and 500 mg/L in the KSLS and KLS samples respectively. Therefore, using a lower dosage of these natural coagulants is better than using a higher dosage. Using a lower dosage can also decrease the organic matter load in wastewater, which will, in turn, benefit the process of economy because a high organic load may lead to microbial growth (Ŝćiban et al., 2009). Underdosing can results in high turbidity and colour levels in the water, whereas overdosing may results in the re-dispersion of impurities and the carryover of polymers from the clarifier to the filtration stage, which will, in turn, result in a blinded filter and a low water yield (Bolto and Gregory, 2007; Veal, 1990).

Tables 4.9 and 4.10 simplify the results presented in Tables 4.7 and 4.8. The ranges were presented in terms of low (L), medium (M), and high (H) RE of the measured parameters. The removal ranges of each group for SS, turbidity, and colour can be categorized as (i) low (L): 0%–40%, (ii) medium (M): 41%–80%, and (iii) high (H): 81%–100%. Given that the REs of COD and NH_3-N in this study were low, another set of categories was introduced, in which low (L) ranged between 0% and 30%, medium (M) ranged between 31% and 60%, and high (H) ranged between 61% and 80%.

Table 4.7: Removal efficiency at optimum conditions for KSLS

	Removal (%)				
Operating Conditions	T_R= 3 min, ω_R=200 rpm T_S= 20 min ω_S= 20 rpm T_{set}= 30 min	T_R= 3 min, ω_R=200 rpm T_S= 20 min ω_S= 40 rpm T_{set}= 50 min	T_R= 3 min, ω_R=200 rpm T_S= 20 min ω_S= 40 rpm T_{set}= 50 min	T_R= 3 min, ω_R=200 rpm T_S= 20 min ω_S= 40 rpm T_{set}= 50 min	T_R= 4 min, ω_R=250 rpm T_S= 20 min ω_S= 30 rpm T_{set}= 40 min
Parameter	PACI 2000 mg/L (pH 6)	DEaqs 1000 mg/L (pH 6)	DEaqs 1000 mg/L (pH 8)	DEaqs 1000 mg/L (pH 10)	DEpowd 1000 mg/L (pH 10)
SS	82	63	74	75	72
Turbidity	83	67	69	74	66
Colour	91	23	55	44	36
COD	53	27	44	36	39
Ammonia-N	38	26	29	69	37

Table 4.8: Removal efficiency at optimum conditions for KLS

	Removal (%)				
Operating Conditions	T_R= 3 min, ω_R=150 rpm T_S= 10 min ω_S= 20 rpm T_{set}= 30 min	T_R= 3 min, ω_R=200 rpm T_S= 15 min ω_S= 30 rpm T_{set}= 40 min	T_R= 3 min, ω_R=200 rpm T_S= 15 min ω_S= 30 rpm T_{set}= 40 min	T_R= 3 min, ω_R=200 rpm T_S= 15 min ω_S= 30 rpm T_{set}= 40 min	T_R= 4 min, ω_R=250 rpm T_S= 20 min ω_S= 30 rpm T_{set}= 40 min
Parameter	PACI 500 mg/L (pH 6)	DEaqs 200 mg/L (pH 4)	DEaqs 200 mg/L (pH 10)	DEaqs 200 mg/L (pH 12)	DEpowd 200 mg/L (pH 10)
SS	90	91	73	94	72
Turbidity	88	91	75	92	66
Colour	90	67	51	48	36
COD	80	69	73	62	39
Ammonia-N	31	22	38	43	37

Table 4.9: Classification of removal efficiency at optimum conditions for KSLS

Parameter	PACI 2000 mg/L (pH 6)	DEaqs 1000 mg/L (pH 6)	DEaqs 1000 mg/L (pH 8)	DEaqs 1000 mg/L (pH 10)	DEpowd 1000 mg/L (pH 10)
SS	H	M	M	M	M
Turbidity	H	M	M	M	M
Colour	H	L	M	M	L
COD	M	L	M	M	M
Ammonia-N	M	L	L	H	M

*(L)-low , (M) – medium, (H)-high

Table 4.10: Classification of removal efficiency at optimum conditions for KLS

Parameter	PACI 500 mg/L (pH 6)	DEaqs 200 mg/L (pH 4)	DEaqs 200 mg/L (pH 10)	DEaqs 200 mg/L (pH 12)	DEpowd 200 mg/L (pH 10)
SS	H	H	M	H	M
Turbidity	H	H	M	H	M
Colour	H	M	M	M	L
COD	H	H	H	H	M
Ammonia-N	M	L	M	M	M

*(L)-low , (M) – medium, (H)-high

Tables 4.7 to 4.10 show that DEaqs has better performance in reducing SS and turbidity in the KLS sample at pH 4. This coagulant was not as effective in the KSLS sample because of the different leachate characteristics in both sites (Section 4.2). An analysis on the CA of DEaqs (Sections 4.6.2.1 to 4.6.2.4) demonstrated that DEaqs and DEpowd coagulant was not inert to pH changes. Furthermore, DEaqs continuously demonstrated high RE at a pH value over 10 in the KLS sample.

A further analysis in Sections 4.6.2.1 to 4.6.2.4 showed that the optimum dosage of DEaqs in the KLS sample should be 200 mg/L (Table 4.8). Tables 4.8 and 4.10 show that the SS and turbidity RE of DEaqs can best that of PACl by 94% and 92% respectively using a dosage of 200 mg/L at pH 12. On other hand, in KSLS,

DEaqs and DEpowd demonstrated low removal rates for all measured parameters compared to a 2000 mg/L dosage of PACl at pH 6 (Table 4.9). However, the NH_3-N RE (69%) of a 1000 mg/L dosage of DEaqs at pH 10 bested that of PACl (38%) (Table 5.8) In the case of polymers, the selection of an optimum pH value was dependent on the initial pH range of the landfill leachates and on the CA equation. Despite demonstrating positive results in terms of RE and CA, DEaqs and DEpowd could also act as coagulants at different pH values and suppress PACl dosages. The dosages of DEaqs and DEpowd in the KLS and KSLS samples were also lower than those of PACl.

4.7 DEaqs and DEpowd as Coagulant Aids

In this case, the coagulant aid can be added after the coagulant to hasten reactions, produce a denser floc, and reduce the required amount of primary coagulant. This section determines the effects of DEaqs and DEpowd as coagulant aid on the removal of turbidity, colour, COD, and NH_3-N from landfill leachates, as well as investigates the effect of natural coagulant on floc structure in the presence of PACl.

4.7.1 Effect of Removal Efficiency

In a dual coagulant system, the inorganic coagulant promotes the destabilization of colloids through charge neutralization, while the polymer or polyelectrolyte can act as a bridging element that accelerates the formation of flocs that can settle more easily, thereby improving the performance of the coagulation–

flocculation process. In this study, the application of PACl at optimum conditions and at two different dosages (2000 and 1000 mg/L in the KSLS sample, and 500 and 200 mg/L in the KLS sample) was compared simultaneously with that of DEaqs and DEpowd, which reduced the amount of PACl by about 50% and 60% respectively. Figures 4.32 to 4.36 (see Appendix E (b)) show the SS, turbidity, colour, COD, and NH_3-N RE of DEaqs and DEpowd in the KLS sample.

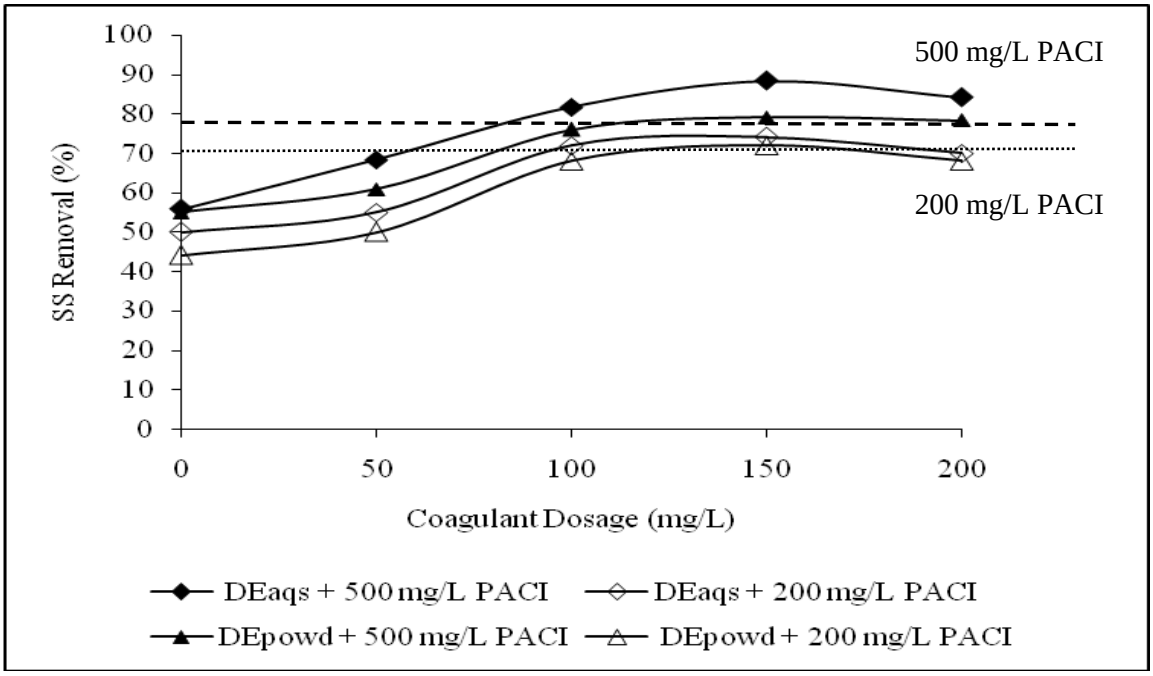

Figure 4.32: SS removal with addition of DEaqs and DEpowd at different concentration in KLS

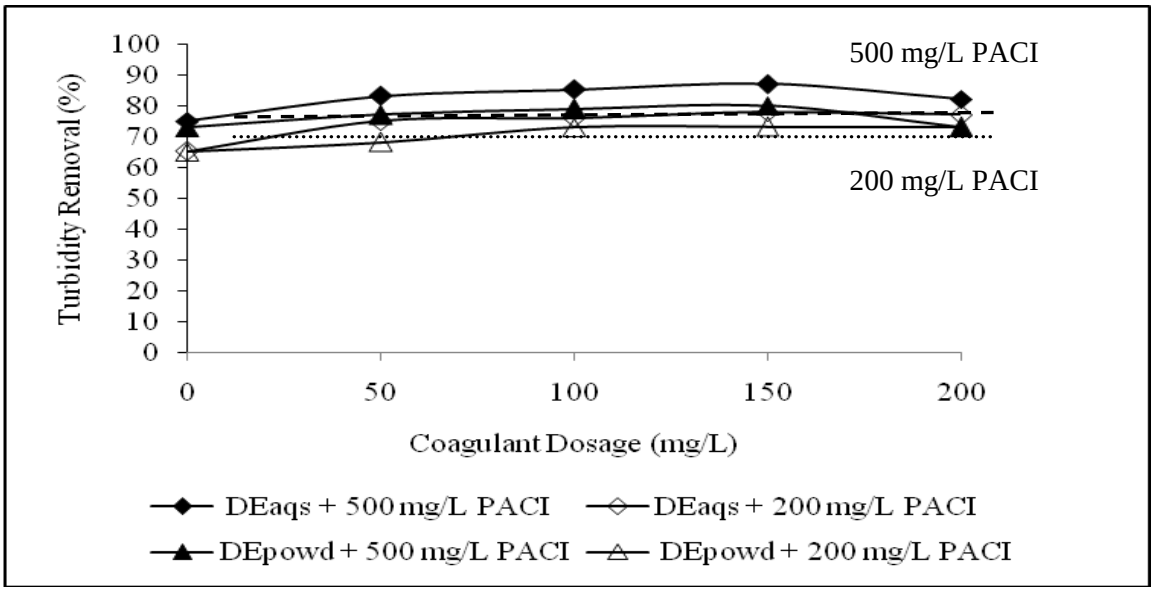

Figure 4.33: Turbidity removal with addition of DEaqs and DEpowd at different concentration in KLS

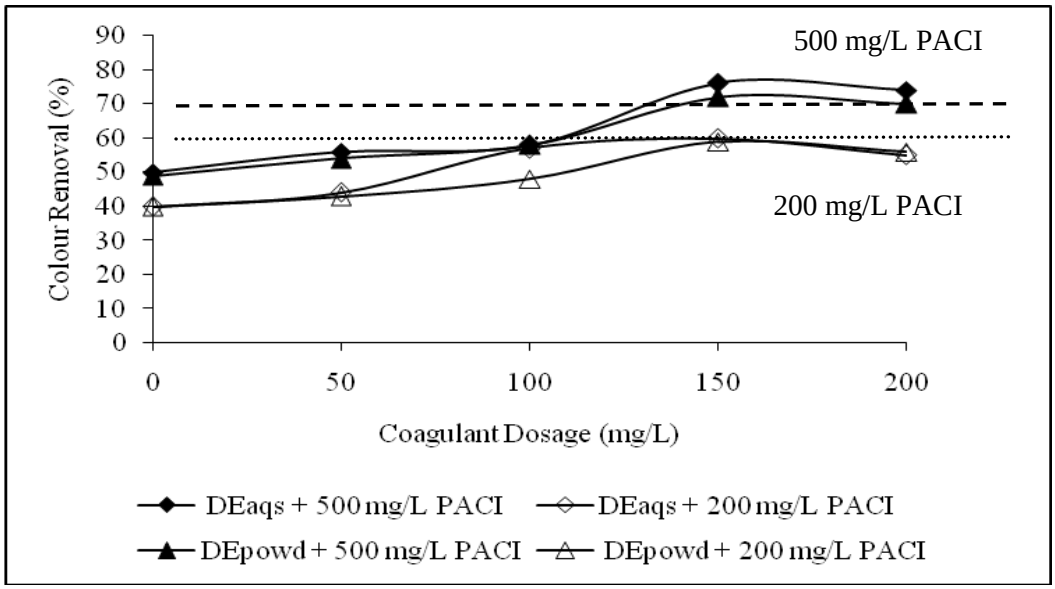

Figure 4.34: Colour removal with addition of DEaqs and DEpowd at different concentration in KLS

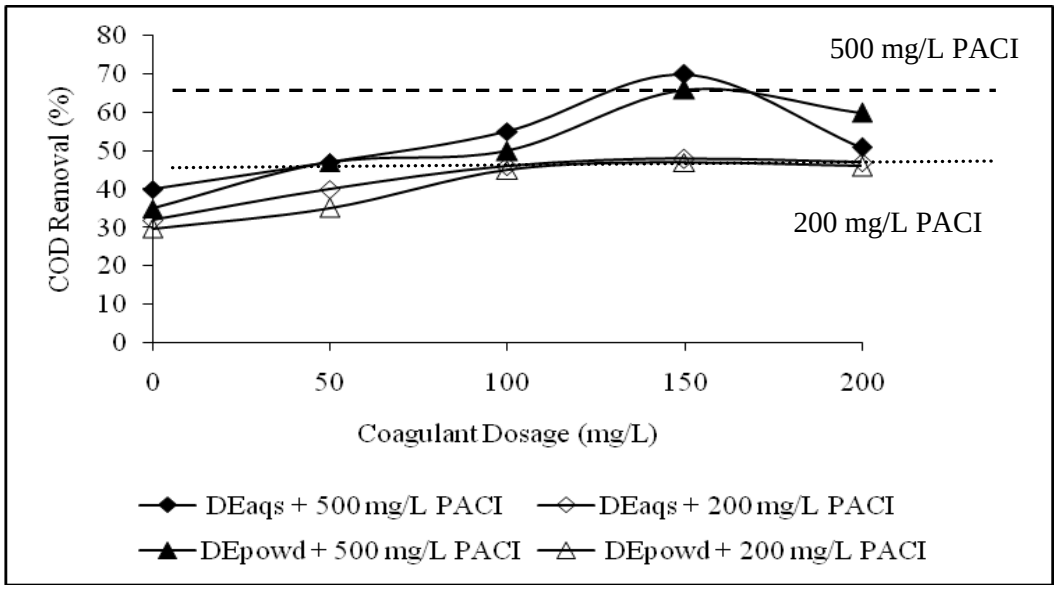

Figure 4.35: COD removal with addition of DEaqs and DEpowd at different concentration in KLS

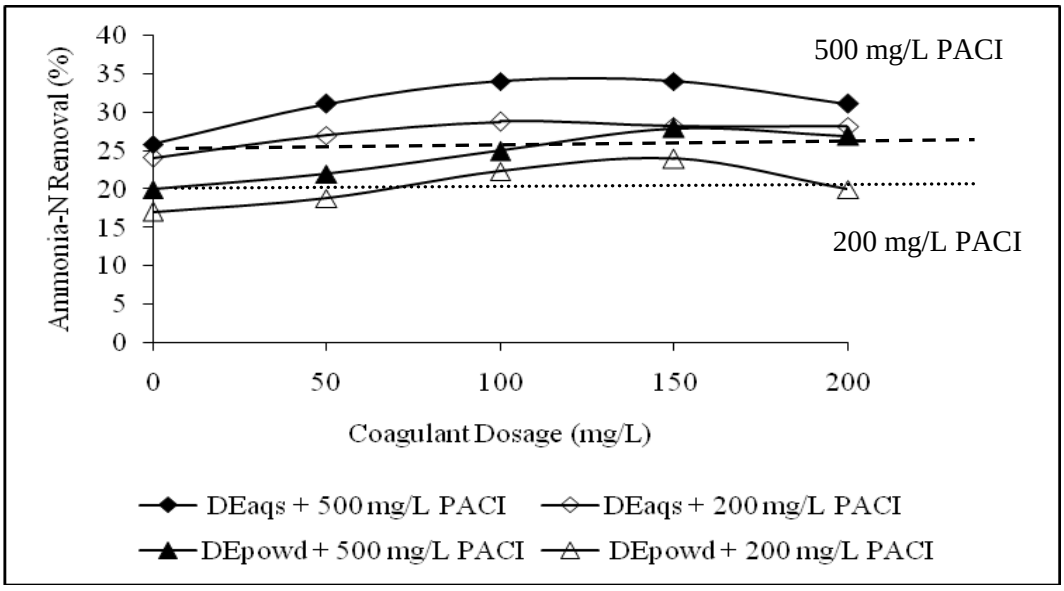

Figure 4.36: Ammonia-N removal with addition of DEaqs and DEpowd at different concentration in KLS

Table 4.11 compares the highest RE of DEaqs with that of DEpowd (Figures 4.32 to 4.36) as coagulant aids in the KLS sample. DEaqs and DEpowd both demonstrated a favorable RE in the KLS sample. The RE was also increased when these two coagulant aids were used than when using PACl alone.

Table 4.11: Removal efficiency with PACI alone, and in conjunction with DEaqs and DEpowd as coagulant aid in KLS

	Removal (%)					
Operating Conditions	T_R= 3 min, ω_R=150rpm T_S= 10 min, ω_S= 20 rpm T_{set}=30 min, pH 6					
Parameter	200 mg/L PACI alone	200 mg/L PACI + 100 mg/L DEaqs	200 mg/L PACI + 100 mg/L DEpowd	500 mg/L PACI alone	500 mg/L PACI + 150 mg/L DEaqs	500 mg/L PACI + 150 mg/L DEpowd
SS	70	72	68	78	88	79
Turbidity	68	76	73	76	87	80
Colour	60	57	48	70	76	71
COD	45	46	45	65	68	66
Ammonia-N	20	29	22	25	34	28

Table 4.11 shows that the addition of 100 mg/L DEaqs and DEpowd in conjunction with 200 mg/L PACl can increase the removal rates. However, a higher dosage of DEaqs and DEpowd (150 mg/L) was needed when the PACl dosage was increased to 500 mg/L. Increasing the PACl dosage also increased the concentration of various hydrolysis species and the number of cationic patches. Therefore, the DEaqs and DEpowd dosages should be increased to bridge and occupy those cationic patches. The addition of DEaqs and DEpowd as coagulant aids in the KLS sample successfully increased the RE of all measured parameters. However, reducing PACl by 60% was proven inefficient for the studied parameters. An average NH_3-N RE

was obtained when the PACl dosage was reduced and when the RE of such coagulant was around ± 2% to 6% and ± 0% to 8% of that of DEaqs and DEpowd respectively. DEaqs was more effective than DEpowd in acting as a coagulant aid in the KLS sample.

Figures 4.37 to 4.41 (see Appendix E (a)) illustrate the efficiency of DEaqs and DEpowd in removing SS, turbidity, colour, COD, and NH_3-N in the KSLS sample. Table 4.23 summarizes the results from Figures 4.37 to 4.41, which show the highest RE of DEaqs and DEpowd as coagulant aids in the KSLS sample.

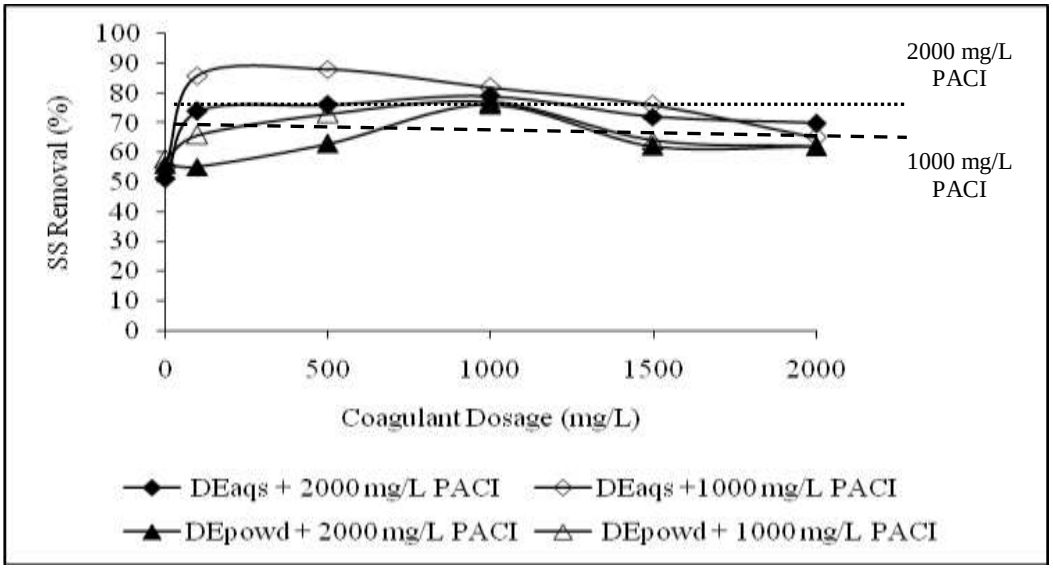

Figure 4.37: SS removal with addition of DEaqs and DEpowd at different concentration in KSLS

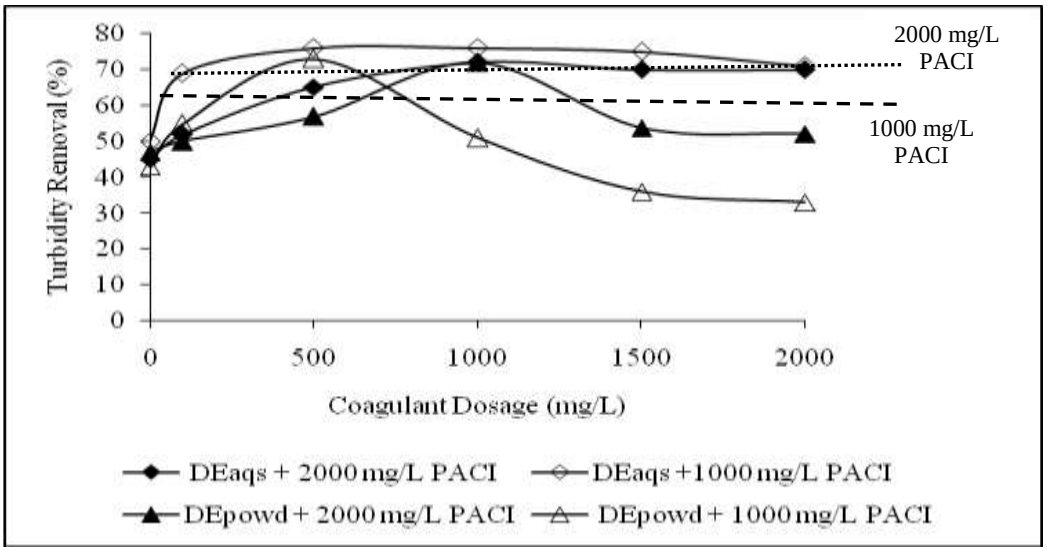

Figure 4.38: Turbidity removal with addition of DEaqs and DEpowd at different concentration in KSLS

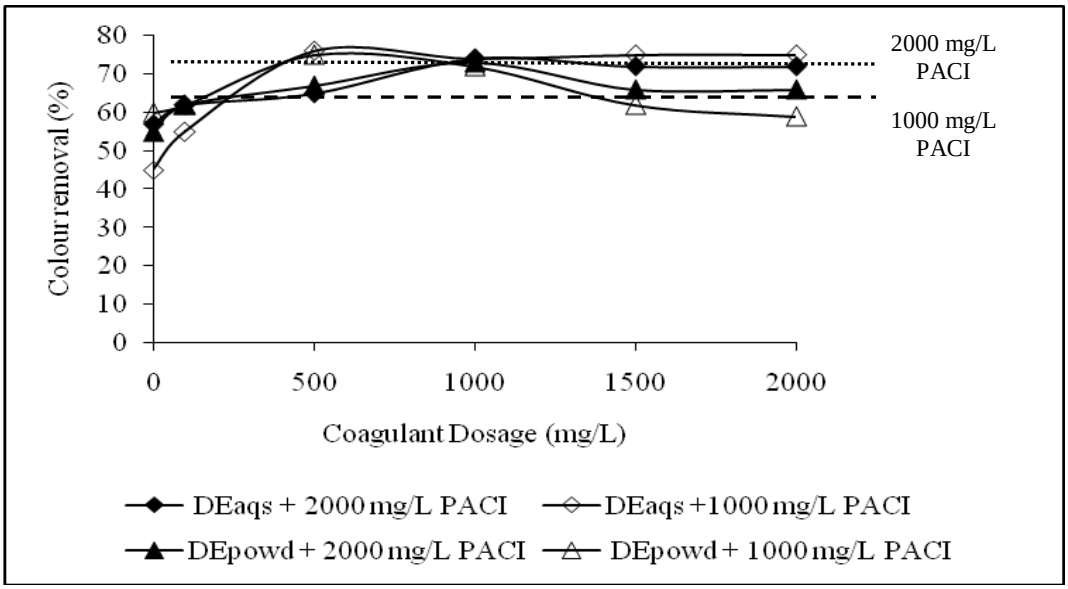

Figure 4.39: Colour removal with addition of DEaqs and DEpowd at different concentration in KSLS

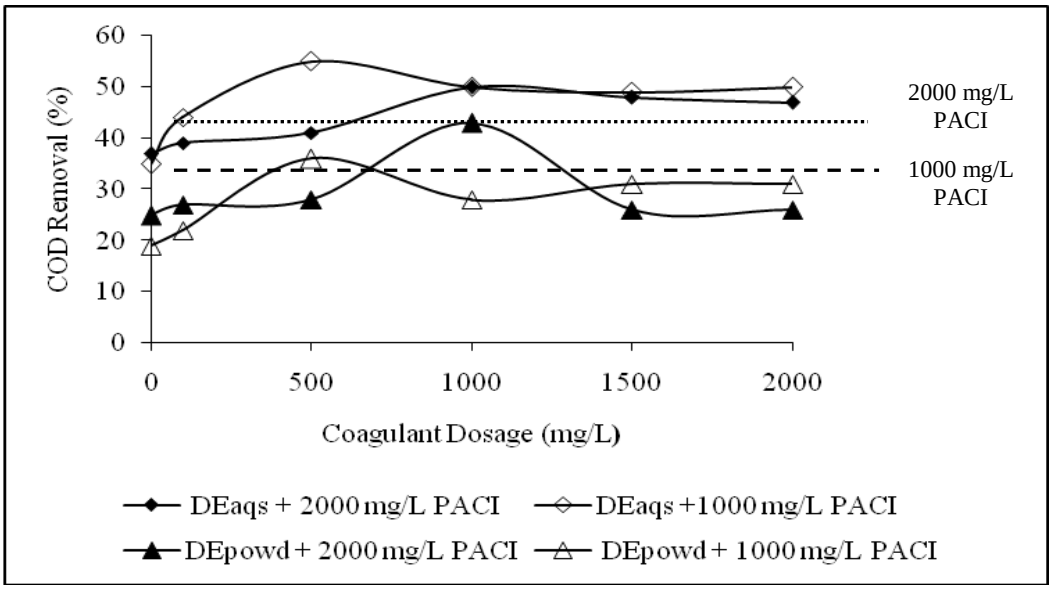

Figure 4.40: COD removal with addition of DEaqs and DEpowd at different concentration in KSLS

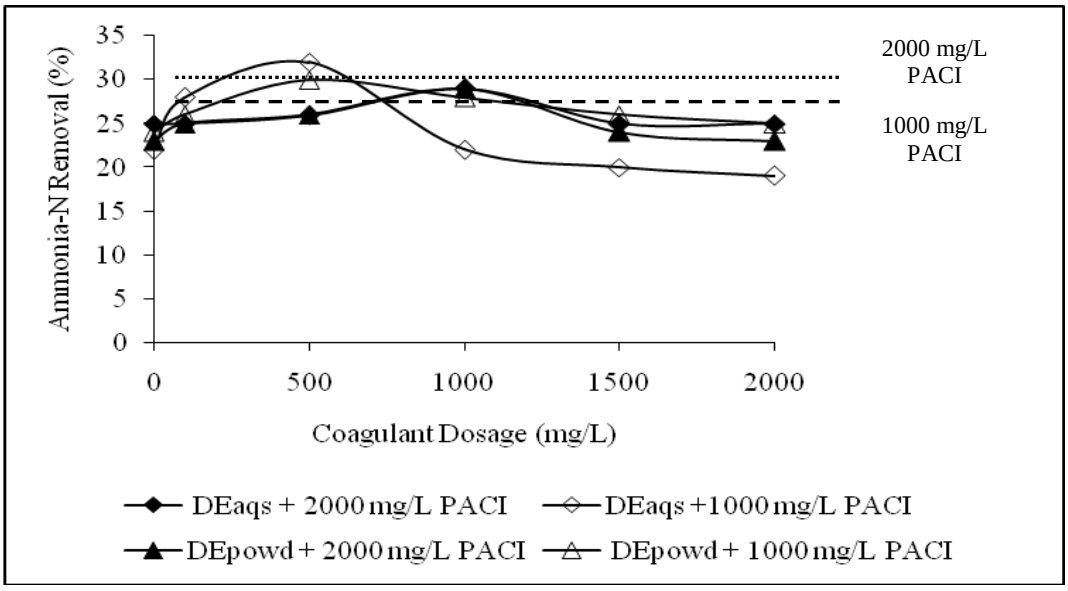

Figure 4.41: Ammonia-N removal with addition of DEaqs and DEpowd at different concentration in KSLS

Table 4.12: Removal efficiency with PACI alone, and in conjunction with DEaqs and DEpowd as coagulant aid in KSLS

	Removal (%)					
Operating Conditions	T_R= 3 min, ω_R= 200 rpm T_S= 20 min, ω_S= 20 rpm T_{set} = 30 min, pH 6					
Parameter	1000 mg/L PACI alone	1000 mg/L PACI + 500 mg/L DEaqs	1000 mg/L PACI + 500 mg/L DEpowd	2000 mg/L PACI alone	2000 mg/L PACI + 1000 mg/L DEaqs	2000 mg/L PACI + 1000 mg/L DEpowd
SS	70	88	73	76	79	76
Turbidity	63	76	73	70	72	74
Colour	68	76	75	72	74	74
COD	35	55	45	42	50	43
Ammonia-N	28	32	30	30	29	29

Figures 4.37 to 4.41 show that the addition of DEaqs and DEpowd at dosages below 1000 mg/L enhances the RE of all studied parameters more than using PACl alone in the KSLS sample. For instance, the combination of 500 mg/L DEaqs and 1000 mg/L PACl removed 88% and 76% of SS and turbidity respectively, whereas 1000 mg/L PACl only removed 70% and 63% of these elements. The SS and turbidity RE of DEaqs and DEpowd became relatively low and constant when their dosages exceeded 1000 mg/L. This observation could be attributed to the saturation of the DEaqs and DEpowd bridge sites, which occupied the surface of the particle for the attachment of segments with interparticle bridges, as well as restabilized the colloidal particulates when the coagulants were used at dosages that exceeded the optimum value (Awang and Aziz, 2012; Ghafari et al., 2010; Aziz et al., 2004; Jarvis et al., 2004). The adsorbed layers could have also caused steric repulsion (Awang and Aziz, 2012; Ersoy, 2005).

The highest NH_3-N RE of the 1000 mg/L PACl and 500 mg/L DEaqs combination was 32% (Figure 4.49), which was 4% greater than that when using 1000 mg/L PACl alone in the KSLS sample. However, Table 4.8 shows that DEaqs can effectively remove NH_3-N in the KSLS sample when used as the primary coagulant at pH 10. This result was consistent with that obtained by previous researchers who argued that higher pH values are optimal for other natural coagulants, such as natural stone powder (Basaran and Tasdedemir, 2014), chestnut and acorn (Ŝćiban et al., 2009), *C. opuntia* (Zhang et al., 2006), *M. oleifera* (Okuda et al., 2001a and 2001b), and *P. juliflora and Cactus latifaria* (Diaz et al., 1999). A 1000 mg/L dosage of DEaqs demonstrated the highest RE of 69% in the KSLS sample. Moreover, the lowest amount of NH_3-N was retained in the samples when PACl was used as the primary coagulant. However, Tables 4.11 and 4.12 shows that the overall percentage of removed NH_3-N was lowest compared to that of other parameters in both samples. This observation could be attributed to the chemical compositions of the *D. esculentum* leaves, which contain a high percentage of nitrogen as mentioned in Section 2.12. Therefore, nitrogen may significantly interfere with the coagulation process.

Figures 4.37 to 4.41 show that 88%, 76%, 76%, 55%, and 32% of SS, turbidity, colour, COD, and NH_3-N were removed by using a combination of 1000 mg/L PACl and 500 mg/L DEaqs. These removal percentages are greater than that when using 2000 mg/L PACl alone, which removed 76%, 70%, 72%, 42%, and 30% of SS, turbidity, color, COD, and NH_3-N, respectively. Therefore, the SS, turbidity, colour, COD, and NH_3-N in the KSLS sample can be successfully removed by

reducing the PACl dosage by approximately 50% and by combining this coagulant with 500 mg/L DEaqs and DEpowd.

4.7.2 Effect on Floc Strength and Breakage

Particle aggregation is an important process that affects the fate of flocs in the coagulation–flocculation process. The properties of aggregated particles, including their size, shape, and strength, substantially affect their removal via gravity sedimentation (O'Melia, 1998).

As indicated in Section 4.7.1, 2000 mg/L PACl, 2000 mg/L PACl + 1000 mg/L DEaqs, and 1000 mg/L PACl + 500 mg/L DEaqs were used to examine the formation, breakage, and regrowth of flocs in the KSLS sample. As mentioned in Section 3.7, the repetition of floc formation and breakage was conducted in three phases (Phase 1, Phase 2, and Phase 3). Tables 4.13 and 4.14 (Appendix E (c)) show the floc sizes at different dosages.

Floc strength is dependent upon the interparticle bonds between components of the aggregate (Bache et al., 1997; Parker et al., 1972). However, flocs may be exposed to a range of stresses. A floc will break if the stress that is applied on its surface is greater than the bonding strength within the floc (Boller and Blaser, 1998). Therefore, strength factor (SF) indicates the ability of flocs to prevent being broken into smaller particles by a certain velocity gradient.

A high SF indicates the low sensitivity of flocs to breakage from increased shear rate. Therefore, flocs with a high SF are stronger than those with low SF. RF

indicates the capacity of flocs to regrow. As reported by Wei et al. (2010) and Xu et al. (2009), flocs with a large RF have a better capability to regrow after shearing.

Tables 4.13 and 4.14 show that the SR and RF of PACl sequentially decreased from Phase 1 to Phase 3. Based on their RF, the flocs formed by using 2000 mg/L PACl + 1000 mg/L DEaqs demonstrated a consistent reformation capacity (Table 4.14). The flocs formed by using 1000 mg/L PACl + 500 mg/L DEaqs demonstrated a higher SF and a better ability to resist shear under the same conditions.

Table 4.13: Floc size at different coagulants combinations

Phase		Diameter (μm)		
		2000 mg/L PACI	2000 mg/L PACI + 1000 mg/L DEaqs	1000 mg/L PACI + 500 mg/L DEaqs
1st	$Size_1$	27.22	26.15	22.81
	$Size_2$	25.92	27.43	28.28
	$Size_3$	24.85	27.93	27.37
2nd	$Size_2$	24.60	28.98	28.10
	$Size_3$	23.55	29.41	28.30
3rd	$Size_2$	23.42	29.25	27.60
	$Size_3$	23.15	29.03	27.35

*Size refers to floc diameter (μm) and denoted by $D_{0.5}$

Table 4.14: Strength and recovery factors of flocs

Phase		2000 mg/L PACI	2000 mg/L PACI + 1000 mg/L DEaqs	1000 mg/L PACI + 500 mg/L DEaqs
1st	SF	95	105	124
	RF	91	107	120
2nd	SF	90	111	123
	RF	87	112	124
3rd	SF	86	112	121
	RF	85	111	120

*SF: Strength Factor *RF: Recovery Factor

When the shear rate increases above the critical level, the flocs will break until a new steady state is reached (Jarvis et al., 2005). However, the flocs will not regrow to their original sizes in a steady phase (Xu et al., 2009) because of the irreversible nature of their breakage. The flocs formed by using 2000 mg/L PACl were unable to regrow after they were broken at a high shear rate in the second and third phases. The high shear rate will also break those flocs with low regrowth capacity even after the addition of polymer in most coagulants (Jarvis et al., 2006).

Table 4.14 shows that reducing the PACl dosage by 50% strengthens the flocs formed in the KSLS sample. The polymer only functions partially under conditions with low or high agitation intensity because of the inhomogeneous distribution of the polymers. The flocs break apart at a high shear rate, and such breakage occurs at the polymer–particle bonds and not at the –C–C– bond of the polymer chain because of their relative bond strengths that hold the floc together. This finding coincides with that of Jarvis et al. (2005) and Yarar (2001).

4.7.3 Sediment Percentage

Aside from determining floc formation, breakage, and regrowth, the sludge that was produced during the treatment of the KSLS sample was examined based on SP. The amount and characteristics of the produced sludge play important roles in the coagulation–flocculation process and are affected by the selection of coagulants as well as by the operating conditions of the coagulation–flocculation process (Aguilar et al., 2005). Therefore, the abundant amount of sludge produced by using chemical coagulants in the coagulation–flocculation process poses a serious problem to operators, who are yet to determine effective ways to handle such sludge. The mishandling of chemical sludge will deteriorate environmental quality (Anselme et al., 1995). Figure 4.49 shows the results of the sludge experiment (Appendix E (d)).

Figure 4.42 shows a small difference between the SP values of PACl (2000 mg/L) and those of PACl (2000 mg/L) + DEaqs (1000 mg/L), with SP values of 36% and 30% respectively. Such difference was attributed to the sludge volume, which was subsequently proportional to PACl dosage. A lower SP value of 25% was observed when the PACl dosage was reduced to 1000 mg/L in combination with 500 mg/L DEaqs.

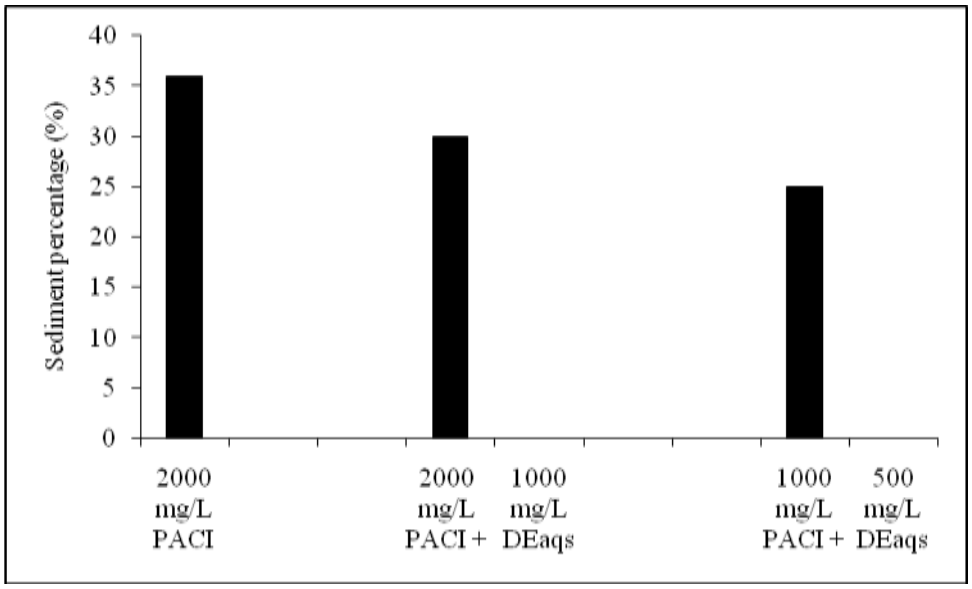

Figure 4.42: Sludge produced with the different combination of coagulant dosage

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This study successfully examined the treatment of landfill leachates by using DEaqs and DEpowd as coagulant aid in the coagulation–flocculation process. PACl was used as a benchmark to measure the removal levels of turbidity, SS, colour, COD and ammonia-N. Before that, DEaqs and DEpowd were also examined for their usefulness as primary coagulant. Leachates from KSLS and KLS were used for the experiments. These leachates were considered stabilized on the basis of their characteristics. The conclusions are summarized as follows:

i. Both DEaqs and DEpowd had been successfully produced from *D.esculentum* leaf using extraction via distilled water and acid treated, respectively. By having a negative surface particle, DEaqs (IEP 4) and DEpowd act as anionic coagulants and are capable of promoting coagulation in landfill leachates that are saturated with negative particles. Their coagulation was facilitated by bridging. While from Debye plot, the molecular weight of DEaqs and DEpowd is 221 kDa and 275 kDa, respectively. It can be concluded that DEaqs and DEpowd as a high molecular weight anionic polymer.They carried functional groups like carboxyl, hydroxyl, and amine groups, all of which were salient for coagulation efficiency.

ii. DEaqs and DEpowd require greater mixing speed and time compared to PACl in both KLS and KSLS samples. For instance, PACl required agitation at a rapid mixing speed (ω_R = 150 rpm) and time (T_R = 3 min) to achieve an optimum hydrolysis process in the KLS sample, whereas DEpowd required a relatively higher mixing speed (ω_R = 250 rpm) and time (T_R = 4 min) in KSLS sample. The settling time (T_{SET}) of flocs by using PACl (30 min) was also faster than by using DEpowd (40 min). It can be revealed that sample with higher concentration level of pollutants (KSLS) required higher mixing speed and contact time compared to KLS sample.The selection of optimum parameters were based on the highest removal of SS, colour, COD and NH_3-N from KLS and KSLS samples.

iii. A 200 mg/L dosage of DEaqs and DEpowd was considered optimal in the KLS sample. Using 200 mg/L DEaqs at pH 12 demonstrated greater RE by removing 94%, 92%, and 43% of SS, turbidity, and NH_3-N, respectively. In contrast, using 500 mg/L PACl at pH 6 only removed 90%, 88%, and 31% of SS, turbidity, and NH_3-N, respectively. An optimum RE was achieved in the KSLS sample by using 1000 mg/L DEaqs and DEpowd at pH 10. DEaqs and DEpowd demonstrated a lower RE for all measured parameters compared to 2000 mg/L PACl at pH 6 in the KSLS sample. Using 1000 mg/L DEaqs at pH 10, DEaqs could achieve a higher NH_3-N removal (69%) compared to PACl (38%) in the KSLS sample. Therefore, DEaqs could be used as a coagulant to reduce NH_3-N in landfill leachates.

As coagulant aids, the addition of DEaqs and DEpowd increased the removal of all studied parameters in the KLS sample. Using a combination of these two coagulants resulted in a higher RE compared to using PACl alone. Using a combination of 1000 mg/L PACl and 500 mg/L DEaqs removed 88%, 76%, 76%, 55%, and 32% of SS, turbidity, colour, COD, and NH_3-N, respectively, from the KSLS sample. These percentages were greater than those achieved by using 2000 mg/L PACl alone (76%, 70%, 72%, 42%, and 30% for SS, turbidity, colour, COD, and NH_3-N, respectively).

iv. Reducing the PACl dosage by 50% from the optimum amount, as well as combining this coagulant with DEaqs and DEpowd with dosages below 1000 mg/L, exhibited a good removal rate on all measured parameters in the KSLS sample.

v. The flocs that were formed by using a combination of 2000 mg/L PACl and 1000 mg/L DEaqs demonstrated a consistently increasing reformation capacity. The RF of these flocs increased up to 112 by using the combination of these coagulants, but decreased to 85 by using PACl alone at the end of the third phase. The flocs that were formed by using a combination of 1000 mg/L PACl and 500 mg/L DEaqs demonstrated better resistance to shear. The SF of these flocs increased up to 121 by using the combination of these coagulants, but decreased to 86 by using PACl alone at the end of Phase 3. The SPs of these flocs were nearly similar when using 2000 mg/L PACl alone and when using a combination of 1000 mg/L DEaqs and 2000 mg/L

PACl. A lower SP of 25% was achieved when the PACl dosage was reduced to 1000 mg/L in combination with 500 mg/L DEaqs.

Although the RE of these coagulants were not as high as that of other established natural, plant-based coagulants such as *M. oleifera*, Fenugreek mucilage, *T. indica* seed mucilage, and *C. opuntia*, this study serves as a starting point for future studies to explore these new types of natural coagulants and to promote them as alternatives to the commercial chemical coagulants in water and wastewater treatment.

5.2 Recommendations for future research

This study presents the following recommendations for future studies:

i. The coagulation activities of DEaqs and DEpowd do not significantly differ from each other. A proper extraction method for synthesizing *D. esculentum* leaves must be developed because *D. esculentum* shows a positive potential to act as a coagulant and to replace the commercial chemical coagulants being sold in the market.

ii. The characteristics of *D. esculentum* leaves must be investigated further, specifically their charge density and viscosity. High Performance Liquid Chromatography can be used to obtain highly detailed percentage compositions of *D. esculentum* leaf extracts.

iii. Future studies must use *D. esculentum* leaf extracts to treat other types of wastewater. These extracts may exhibit higher pollutant RE for

low-strength pollutant concentrations or less-complex waters, such as surface water (i.e., rivers and lakes).

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APPENDICES

APPENDIX A

The example calculation method to determine the amount of coagulant dosages for DEaqs, DEpowd and PACI (18%).

a) DEaqs and DEpowd

Stock solution = 100 g/L (100 000 mg/L)

If 1000 mg/L ,

$M_1V_1 = M_2V_2$

V_1 = (1000 mg/L X 500 mL)) / 100000 mg/L

= 5 mL

b) PACI (18%)

Stock solution = 180 g/L (180 000 mg/L)

If 1000 mg/L ,

$M_1V_1 = M_2V_2$

V_1 = (1000 mg/L X 500 mL)) / 180 000 mg/L = 2.8 mL

APPENDIX B: OPERATING CONDITIONS DATA

1. PACI in KSLS

a. Determination of optimum time for rapid mixing: PACI

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
1	302	42	86	3544	576	84	736	639	13	1640	1070	35
2	302	26	91	3544	555	84	736	660	10	1640	1110	32
3	302	30	90	3544	504	86	736	634	14	1640	850	48
4	302	41	86	3544	569	84	736	649	12	1640	990	40
5	302	33	89	3544	610	83	736	650	12	1640	1100	33
6	302	28	91	3544	609	83	736	638	13	1640	1100	33

b. Determination of optimum speed for rapid mixing: PACI

Speed (rpm)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
70	302	108	64	3544	911	74	736	661	10	1640	1230	25
100	302	88	71	3544	1034	71	736	640	13	1640	1270	23
150	302	107	65	3544	828	77	736	699	5	1640	1330	19
200	302	45	85	3544	785	78	736	651	12	1640	1170	29
250	302	148	51	3544	820	77	736	675	8	1640	1350	18
300	302	107	65	3544	812	77	736	652	11	1640	1640	0

c. Determination of optimum time for slow mixing: PACI

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
5	302	36	88	3544	649	82	736	705	4	1640	1170	29
10	302	36	88	3544	667	81	736	709	4	1640	1100	33
15	302	24	92	3544	648	82	736	655	11	1640	1170	29
20	302	32	89	3544	683	81	736	633	14	1640	990	40
25	302	11	96	3544	692	80	736	702	5	1640	1190	27
30	302	11	96	3544	666	81	736	672	9	1640	1090	34

d. Determination of optimum speed for slow mixing: PACI

Speed (rpm)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
10	302	44	85	3544	646	82	736	716	3	1640	1070	35
20	302	26	91	3544	632	82	736	696	5	1640	920	44
30	302	30	90	3544	500	86	736	690	6	1640	1030	37
40	302	28	91	3544	614	83	736	677	8	1640	1190	27
50	302	27	91	3544	614	83	736	679	8	1640	1060	35
60	302	45	85	3544	647	82	736	689	6	1640	1200	27

e. Determination of optimum settling time: PACI

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
10	302	74	75	3544	879	75	736	671	9	1640	1120	32
20	302	141	53	3544	913	74	736	664	10	1640	1460	11
30	302	55	82	3544	734	79	736	621	16	1640	1180	28
40	302	87	71	3544	913	74	736	611	17	1640	1070	35
50	302	122	60	3544	851	76	736	587	20	1640	1230	25
60	302	56	81	3544	940	73	736	663	10	1640	1120	32

2. DEaqs in KSLS

a. Determination of optimum time for rapid mixing: DEaqs

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
1	456	126	72	4020	2278	43	870	707	19	1580	970	39
2	456	122	73	4020	2330	42	870	709	19	1580	910	42
3	456	127	72	4020	2183	46	870	743	15	1580	880	44
4	456	126	72	4020	2472	39	870	710	18	1580	960	39
5	456	123	73	4020	2164	46	870	744	14	1580	980	38
6	456	119	74	4020	2286	43	870	677	22	1580	1030	35

b. Determination of optimum speed for rapid mixing: DEaqs

Speed (rpm)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
70	456	135	70	4020	2062	49	870	687	21	1580	900	43
100	456	136	70	4020	2101	48	870	709	19	1580	1379	13
150	456	138	70	4020	2228	45	870	706	19	1580	810	49
200	456	131	71	4020	2114	47	870	696	20	1580	950	40
250	456	135	70	4020	2401	40	870	718	17	1580	1040	34
300	456	135	70	4020	2221	45	870	751	14	1580	1210	23

c. Determination of optimum time for slow mixing: DEaqs

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
5	456	140	69	4020	2198	45	870	737	15	1580	820	48
10	456	138	70	4020	2215	45	870	709	19	1580	1000	37
15	456	137	70	4020	2186	46	870	721	17	1580	1010	36
20	456	136	70	4020	2147	47	870	738	15	1580	880	44
25	456	142	69	4020	2118	47	870	750	14	1580	930	41
30	456	135	70	4020	2173	46	870	723	17	1580	930	41

d. Determination of optimum speed for slow mixing: DEaqs

Speed (rpm)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
10	456	132	71	4020	2277	43	870	737	15	1580	730	54
20	456	134	71	4020	2301	43	870	736	15	1580	910	42
30	456	133	71	4020	2366	41	870	760	13	1580	1260	20
40	456	134	71	4020	2260	44	870	737	15	1580	920	42
50	456	136	70	4020	2138	47	870	730	16	1580	870	45
60	456	144	68	4020	2584	36	870	739	15	1580	1080	32

e. Determination of optimum settling time: DEaqs

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
10	456	184	60	4020	2553	36	870	755	13	1580	920	42
20	456	184	60	4020	2847	29	870	744	14	1580	930	41
30	456	171	63	4020	2713	33	870	744	14	1580	820	48
40	456	153	66	4020	2791	31	870	740	15	1580	940	41
50	456	138	70	4020	2108	48	870	732	16	1580	820	48
60	456	152	67	4020	2008	50	870	757	13	1580	740	53

3. DEpowd in KSLS

a. Determination of optimum time for rapid mixing: DEpowd

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
1	180	90	50	2400	2100	13	843	760	10	2040	1900	7
2	180	87	52	2400	2000	17	843	744	12	2040	1800	12
3	180	65	64	2400	1990	17	843	700	17	2040	1750	14
4	180	50	72	2400	1800	24	843	614	27	2040	1600	22
5	180	68	62	2400	1990	17	843	620	26	2040	1660	19
6	180	68	66	2400	2000	17	843	630	25	2040	1700	17

b. Determination of optimum speed for rapid mixing: DEpowd

Speed (rpm)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
70	180	52	71	2400	2310	4	843	650	23	2040	2000	2
100	180	46	74	2400	2100	13	843	640	24	2040	1700	17
150	180	40	78	2400	1965	18	843	630	25	2040	1650	19
200	180	35	81	2400	1900	21	843	610	28	2040	1600	22
250	180	32	82	2400	1750	27	843	600	29	2040	1550	24
300	180	42	77	2400	1900	21	843	650	23	2040	1660	19

c. Determination of optimum time for slow mixing: DEpowd

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
5	180	36	80	2400	2300	4	843	666	21	2040	2000	2
10	180	36	80	2400	2000	17	843	660	22	2040	1800	12
15	180	34	81	2400	1995	17	843	630	25	2040	1700	17
20	180	32	82	2400	1666	31	843	614	27	2040	1550	24
25	180	34	81	2400	1768	26	843	621	26	2040	1780	13
30	180	36	80	2400	1880	22	843	620	26	2040	1780	13

d. Determination of optimum speed for slow mixing: DEpowd

Speed (rpm)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
10	180	50	72	2400	2210	8	843	646	23	2040	1770	13
20	180	46	74	2400	2010	16	843	632	25	2040	1500	26
30	180	44	76	2400	1600	33	843	500	41	2040	1440	29
40	180	47	74	2400	1700	29	843	614	27	2040	1668	18
50	180	47	74	2400	1750	27	843	614	27	2040	1700	17
60	180	49	73	2400	1889	21	843	647	23	2040	1880	8

e. Determination of optimum settling time: DEpowd

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
10	180	65	64	2400	2200	8	843	767	9	2040	1800	12
20	180	63	65	2400	2000	17	843	747	11	2040	1500	26
30	180	55	69	2400	1890	21	843	703	17	2040	1520	25
40	180	55	69	2400	1850	23	843	610	28	2040	1450	29
50	180	56	69	2400	1900	21	843	640	24	2040	1670	18
60	180	58	68	2400	1960	18	843	640	24	2040	1780	13

4. PACI in KLS

a. Determination of optimum time for rapid mixing: PACI

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
1	125	12	90	432	52	88	103	53	49	280	235	16
2	125	12	90	432	36	92	103	59	43	280	215	23
3	125	12	90	432	32	93	103	49	52	280	220	21
4	125	11	91	432	35	92	103	61	41	280	215	23
5	125	14	89	432	37	91	103	73	29	280	220	21
6	125	13	90	432	35	92	103	59	43	280	245	13

b. Determination of optimum speed for rapid mixing: PACI

Speed (rpm)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
70	125	11	91	432	47	89	103	77	25	280	88	69
100	125	12	90	432	41	91	103	60	42	280	95	66
150	125	13	90	432	44	90	103	61	41	280	80	71
200	125	11	91	432	47	89	103	69	33	280	90	68
250	125	12	90	432	47	89	103	60	42	280	80	71
300	125	12	90	432	46	89	103	88	15	280	95	66

c. Determination of optimum time for slow mixing: PACI

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
5	125	12	90	432	51	88	103	78	24	280	90	68
10	125	12	90	432	42	90	103	63	39	280	90	68
15	125	12	90	432	37	91	103	75	27	280	98	65
20	125	12	90	432	44	90	103	77	25	280	80	71
25	125	12	90	432	44	90	103	77	25	280	83	70
30	125	13	90	432	43	90	103	77	25	280	80	71

d. Determination of optimum speed for slow mixing: PACI

Speed (rpm)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
10	125	16	87	432	51	88	103	70	32	280	243	13
20	125	18	86	432	24	94	103	56	46	280	221	21
30	125	17	86	432	28	94	103	64	38	280	209	25
40	125	12	90	432	30	93	103	70	32	280	211	25
50	125	13	90	432	31	93	103	75	27	280	205	27
60	125	14	89	432	25	94	103	73	29	280	209	25

e. Determination of optimum settling time: PACI

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
10	125	18	86	432	56	87	103	64	38	280	183	35
20	125	16	87	432	54	88	103	70	32	280	179	36
30	125	10	92	432	51	88	103	66	36	280	175	38
40	125	14	89	432	56	87	103	70	32	280	209	25
50	125	17	86	432	57	87	103	68	34	280	208	26
60	125	15	88	432	51	88	103	67	35	280	182	35

5. DEaqs in KLS

a. Determination of optimum time for rapid mixing: DEaqs

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
1	50	19	62	264	142	46	190	94	51	280	230	18
2	50	21	58	264	147	44	190	89	53	280	200	29
3	50	19	62	264	121	54	190	72	62	280	150	46
4	50	25	50	264	155	41	190	106	44	280	200	29
5	50	18	64	264	132	50	190	87	54	280	210	25
6	50	17	66	264	118	55	190	83	56	280	220	21

b. Determination of optimum speed for rapid mixing: DEaqs

Speed (rpm)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
70	50	24	52	264	188	29	190	91	52	280	180	36
100	50	25	50	264	148	44	190	87	54	280	170	39
150	50	25	50	264	175	34	190	110	42	280	120	57
200	50	22	56	264	134	49	190	82	57	280	110	61
250	50	22	56	264	153	42	190	97	49	280	190	32
300	50	23	54	264	153	42	190	78	59	280	240	14

c. Determination of optimum time for slow mixing: DEaqs

Time (min)	SS			Color			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
5	50	25	50	264	155	41	190	99	48	280	127	55
10	50	23	54	264	144	45	190	98	48	280	125	55
15	50	18	64	264	154	42	190	91	52	280	133	53
20	50	20	60	264	170	36	190	102	46	280	126	55
25	50	19	62	264	133	50	190	98	48	280	133	53
30	50	23	54	264	157	41	190	110	42	280	157	44

d. Determination of optimum speed for slow mixing: DEaqs

Speed (rpm)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
10	59	17	71	252	159	37	200	130	35	128	74	42
20	59	13	78	252	165	35	200	119	41	128	74	42
30	59	8	86	252	167	34	200	111	45	128	80	38
40	59	12	80	252	135	46	200	118	41	128	79	38
50	59	9	85	252	144	43	200	114	43	128	76	41
60	59	14	76	252	130	48	200	116	42	128	79	38

e. Determination of optimum settling time: DEaqs

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
10	59	12	80	252	129	49	200	109	46	128	70	45
20	59	14	76	252	135	46	200	124	38	128	59	54
30	59	11	81	252	144	43	200	118	41	128	64	50
40	59	8	86	252	125	50	200	101	50	128	63	51
50	59	11	81	252	144	43	200	120	40	128	63	51
60	59	20	66	252	131	48	200	111	45	128	73	43

6. DEpowd in KLS

a. Determination of optimum time for rapid mixing: DEpowd

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
1	123	43	65	799	660	17	294	266	10	145	132	9
2	123	36	71	799	640	20	294	230	22	145	124	14
3	123	34	72	799	620	22	294	216	27	145	125	14
4	123	32	74	799	610	24	294	214	27	145	113	22
5	123	34	72	799	620	22	294	220	25	145	114	21
6	123	40	67	799	640	20	294	221	25	145	118	19

b. Determination of optimum speed for rapid mixing: Dpowd

Speed (rpm)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
70	123	52	58	799	660	17	294	270	8	145	130	10
100	123	46	63	799	640	20	294	266	10	145	128	12
150	123	40	67	799	630	21	294	240	18	145	126	13
200	123	35	72	799	610	24	294	220	25	145	122	16
250	123	32	74	799	600	25	294	210	29	145	115	21
300	123	42	66	799	650	19	294	225	23	145	120	17

c. Determination of optimum time for slow mixing: DEpowd

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
5	123	36	71	799	667	17	294	266	10	145	132	9
10	123	36	71	799	667	17	294	260	12	145	130	10
15	123	34	72	799	648	19	294	230	22	145	125	14
20	123	32	74	799	610	24	294	214	27	145	114	21
25	123	34	72	799	666	17	294	221	25	145	113	22
30	123	36	71	799	692	13	294	220	25	145	118	19

d. Determination of optimum speed for slow mixing: DEpowd

Speed (rpm)	SS			Color			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
10	123	44	64	799	646	19	294	260	12	145	132	9
20	123	30	76	799	632	21	294	230	22	145	124	14
30	123	26	79	799	500	37	294	214	27	145	110	24
40	123	28	77	799	614	23	294	220	25	145	120	17
50	123	27	78	799	614	23	294	222	24	145	128	12
60	123	45	63	799	647	19	294	225	23	145	130	10

e. Determination of optimum settling time: DEpowd

Time (min)	SS			Colour			COD			NH_3-N		
	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %	INITIAL (mg/L)	FINAL (mg/L)	REMOVAL %
10	123	40	67	799	767	4	294	266	10	145	130	10
20	123	36	71	799	747	7	294	230	22	145	125	14
30	123	34	72	799	703	12	294	226	23	145	120	17
40	123	32	74	799	610	24	294	200	32	145	100	31
50	123	32	74	799	640	20	294	220	25	145	114	21
60	123	33	73	799	640	20	294	221	25	145	118	19

APPENDIX C: pH Optimum

(a) Determination of optimum pH in KSLS

1. PACI

pH	SS			Turbidity			Colour		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
2	152	87	43	82.3	46.20	44	1939	812	58
4	152	22	86	82.3	20.50	75	1939	277	86
6	152	20	87	82.3	11.70	86	1939	210	89
8	152	101	34	82.3	35.30	57	1939	1032	47
10	152	110	28	82.3	49.30	40	1939	1513	22
12	152	46	70	82.3	25.10	70	1939	1664	14

pH	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
2	850	684	20	1710	1197	30
4	850	652	23	1710	1180	31
6	850	641	25	1710	1112	35
8	850	657	23	1710	1214	29
10	850	653	23	1710	1214	29
12	850	646	24	1710	1283	25

2. DEaqs

pH	SS			Turbidity			Colour		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
2	495	185	63	235	125.00	47	4030	874	78
4	495	383	23	235	198.00	16	4030	1644	59
6	495	343	31	235	217.00	8	4030	2749	32
8	495	279	44	235	200.00	15	4030	3000	26
10	495	156	68	235	111.00	53	4030	2275	44
12	495	348	30	235	222.00	6	4030	2418	40

pH	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
2	887	782	12	2040	1489	27
4	887	806	9	2040	1367	33
6	887	833	6	2040	1387	32
8	887	766	14	2040	1306	36
10	887	739	17	2040	918	55
12	887	822	7	2040	1081	51

3. DEpowd

pH	SS			Turbidity			Color		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
2	202	76	62	101	37.90	62	2510	2110	16
4	202	67	67	101	37.90	62	2510	1860	26
6	202	41	68	101	35.00	65	2510	1630	35
8	202	41	73	101	34.00	66	2510	1600	36
10	202	34	75	101	33.00	67	2510	1510	40
12	202	35	76	101	35.00	65	2510	1530	39

pH	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
2	843	700	17	2040	1550	24
4	843	640	24	2040	1428	30
6	843	630	25	2040	1367	33
8	843	600	29	2040	1367	33
10	843	500	41	2040	1306	36
12	843	520	38	2040	1346	34

(b) Determination of optimum pH in KLS

1. PACI

pH	SS			Turbidity			Colour		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
2	99	21	79	67	18.20	73	440	78	82
4	99	23	77	67	13.50	80	440	71	84
6	99	12	88	67	10.62	84	440	45	90
8	99	16	84	67	11.08	83	440	51	88
10	99	18	82	67	12.22	82	440	56	87
12	99	19	81	67	12.84	81	440	60	86

pH	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
2	115	100	13	188	141	25
4	115	79	31	188	130	31
6	115	55	52	188	124	34
8	115	64	44	188	122	35
10	115	71	38	188	143	24
12	115	72	37	188	135	28

2. DEaqs

pH	SS			Turbidity			Colour		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
2	125	26	79	64.4	10.50	84	268	137	49
4	125	25	80	64.4	11.90	82	268	145	46
6	125	45	64	64.4	13.50	79	268	153	43
8	125	45	64	64.4	12.60	80	268	153	43
10	125	38	70	64.4	11.10	83	268	131	51
12	125	10	92	64.4	6.12	90	268	134	50

pH	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
2	250	109	56	157	118	25
4	250	122	51	157	115	27
6	250	109	56	157	105	33
8	250	109	56	157	97	38
10	250	111	56	157	91	42
12	250	75	70	157	94	40

3. DEpowd

pH	SS			Turbidity			Colour		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
2	133	76	43	65.1	47.90	26	810	700	14
4	133	67	50	65.1	47.90	26	810	640	21
6	133	41	69	65.1	20.50	69	810	630	22
8	133	41	69	65.1	14.00	78	810	600	26
10	133	28	79	65.1	13.00	80	810	510	37
12	133	35	74	65.1	31.90	51	810	520	36

pH	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
2	310	250	19	178	167	6
4	310	245	21	178	158	11
6	310	225	27	178	150	16
8	310	220	29	178	144	19
10	310	198	36	178	123	31
12	310	200	35	178	144	19

APPENDIX D: Dosage Optimum

(a) Determination of optimum dosage in KSLS

1. PACI

Dosage	SS			Coagulation Activity	Turbidity			Coagulation Activity	Colour			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(NTU)	(NTU)	%		(mg/L)	(mg/L)	%	
0	152	75	51	-	82.3	45.10	45	-	1939	840	57	--
1000	152	29	81	0.61	82.3	30.20	63	0.33	1939	188	90	0.78
2000	152	27	82	0.64	82.3	14.20	83	0.69	1939	180	91	0.79
3000	152	38	75	0.49	82.3	17.90	78	0.60	1939	245	87	0.71
4000	152	70	54	0.07	82.3	36.50	56	0.19	1939	260	87	0.69
5000	152	57	63	0.24	82.3	60.60	26	-0.34	1939	571	71	0.32

Dosage	COD			Coagulation Activity	NH_3-N			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(mg/L)	(mg/L)	%	
0	850	600	29	-	1710	1180	31	-
1000	850	550	35	0.08	1710	1146	33	0.03
2000	850	400	53	0.33	1710	1060	38	0.10
3000	850	420	51	0.30	1710	1094	36	0.07
4000	850	460	46	0.23	1710	1112	35	0.06
5000	850	500	41	0.17	1710	1129	34	0.04

2. DEaqs (pH 6)

Dosage	SS			Coagulation Activity	Turbidity			Coagulation Activity	Colour			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(NTU)	(NTU)	%		(mg/L)	(mg/L)	%	
0	495	230	54	-	235	95.00	60	-	4030	3836	5	-
1000	495	181	63	0.21	235	76.60	67	0.19	4030	3099	23	0.19
2000	495	179	64	0.22	235	74.60	68	0.21	4030	3100	23	0.19
3000	495	182	63	0.21	235	74.00	69	0.22	4030	3400	16	0.11
4000	495	181	63	0.21	235	72.60	69	0.24	4030	3700	8	0.04
5000	495	194	61	0.16	235	81.50	65	0.14	4030	3721	8	0.04

Dosage	COD			Coagulation Activity	NH_3-N			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(mg/L)	(mg/L)	%	
0	887	662	25	-	2040	1693	17	-
1000	887	650	27	0.02	2040	1510	26	0.11
2000	887	686	23	-0.03	2040	1220	40	0.28
3000	887	704	21	-0.06	2040	1250	39	0.26
4000	887	673	24	-0.02	2040	1480	27	0.13
5000	887	677	24	-0.02	2040	1510	26	0.11

3. DEaqs (pH 8)

Dosage	SS			Coagulation Activity	Turbidity			Coagulation Activity	Colour			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(NTU)	(NTU)	%		(mg/L)	(mg/L)	%	
0	495	225	55	-	235	98.00	58	-	4030	2335	42	-
1000	495	131	74	0.42	235	73.90	69	0.25	4030	1796	55	0.23
2000	495	131	74	0.42	235	76.10	68	0.22	4030	1998	50	0.14
3000	495	137	72	0.39	235	79.60	66	0.19	4030	2075	49	0.11
4000	495	129	74	0.43	235	77.00	67	0.21	4030	2332	42	0.00
5000	495	139	72	0.38	235	80.70	66	0.18	4030	2332	42	0.00

Dosage	COD			Coagulation Activity	NH_3-N			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(mg/L)	(mg/L)	%	
0	887	700	21	-	2040	1489	27	-
1000	887	500	44	0.29	2040	1448	29	0.03
2000	887	510	43	0.27	2040	1244	39	0.16
3000	887	520	41	0.26	2040	1346	34	0.1
4000	887	630	29	0.10	2040	1367	33	0.08
5000	887	640	28	0.09	2040	1367	33	0.08

4. DEaqs (pH 10)

Dosage	SS			Coagulation Activity	Turbidity			Coagulation Activity	Colour			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(NTU)	(NTU)	%		(mg/L)	(mg/L)	%	
0	495	221	55	-	235	134.00	43	-	4030	2158	46	-
1000	495	119	76	0.48	235	61.10	74	0.54	4030	2253	44	-0.04
2000	495	124	75	0.47	235	65.80	72	0.51	4030	2337	42	-0.08
3000	495	129	74	0.43	235	70.50	70	o.47	4030	2378	41	-0.10
4000	495	208	58	0.06	235	131.00	44	0.02	4030	2418	40	-0.12
5000	495	213	57	0.03	235	136.00	42	-0.01	4030	2418	40	-0.12

Dosage	COD			Coagulation Activity	NH_3-N			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(mg/L)	(mg/L)	%	
0	887	728	18	-	2040	1200	41	-
1000	887	572	36	0.21	2040	630	69	0.48
2000	887	673	24	0.08	2040	670	67	0.44
3000	877	621	29	0.15	2040	857	58	0.29
4000	877	668	24	0.08	2040	918	55	0.24
5000	877	668	24	0.08	2040	1000	51	0.17

5. DEpowd (pH 10)

Dosage	SS			Coagulation Activity	Turbidity			Coagulation Activity	Colour			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	mg/L	%		(NTU)	(NTU)	%		(mg/L)	(mg/L)	%	
0	202	100	50	-	101	42.00	58	-	2510	1581	37	-
1000	202	57	72	0.43	101	34.00	66	0.19	2510	1600	36	-0.01
2000	202	61	70	0.39	101	34.00	66	0.19	2510	1632	35	-0.03
3000	202	65	68	0.35	101	36.80	64	0.12	2510	1657	34	-0.05
4000	202	69	66	0.31	101	36.90	63	0.12	2510	1657	34	-0.05
5000	202	69	66	0.31	101	38.38	62	0.10	2510	1682	33	-0.06

Dosage	COD			Coagulation Activity	NH_3-N			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(mg/L)	(mg/L)	%	
0	843	598	29	-	2040	1897	7	-
1000	843	514	39	0.14	2040	1285	37	0.32
2000	843	548	35	0.08	2040	1550	24	0.18
3000	843	565	33	0.06	2040	1652	19	0.13
4000	843	573	32	0.04	2040	1775	13	0.06
5000	843	582	31	0.03	2040	1775	13	0.06

(b) Determination of optimum dosage in KLS

1. PACI

Dosage	SS			Coagulation Activity	Turbidity			Coagulation Activity	Colour			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(NTU)	(NTU)	%		(mg/L)	(mg/L)	%	
0	125	60	52	-	64.4	22.40	65	-	795	255	68	-
200	125	15	88	0.56	64.4	10.20	84	0.54	795	101	87	0.60
400	125	12	90	0.65	64.4	5.71	91	0.75	795	66	92	0.74
600	125	18	86	0.47	64.4	11.00	83	0.51	795	78	90	0.69
800	125	16	87	0.53	64.4	18.10	72	0.19	795	88	89	0.65
1000	125	21	83	0.38	64.4	32.10	50	-0.43	795	82	90	0.68

Dosage	COD			Coagulation Activity	NH_3-N			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(mg/L)	(mg/L)	%	
0	197	94	52	-	280	240	27	-
200	197	59	70	0.37	280	199	29	0.17
400	197	36	82	0.60	280	193	31	0.20
600	197	61	69	0.35	280	193	31	0.20
800	197	61	69	0.35	280	204	27	0.15
1000	197	76	61	0.19	280	204	27	0.15

2. DEaqs (pH 4)

Dosage	SS			Coagulation Activity	Turbidity			Coagulation Activity	Colour			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(NTU)	(NTU)	%		(mg/L)	(mg/L)	%	
0	125	20	84	-	64.4	8.36	87	-	268	116	57	-
200	125	11	91	0.45	64.4	5.84	91	0.30	268	89	67	0.23
400	125	12	90	0.40	64.4	5.08	92	0.39	268	107	60	0.08
600	125	14	89	0.30	64.4	5.70	91	0.32	268	117	56	-0.01
800	125	13	90	0.35	64.4	7.62	88	0.74	268	126	53	-0.09
1000	125	17	86	0.15	64.4	7.18	89	0.14	268	138	49	-0.19

Dosage	COD			Coagulation Activity	NH_3-N			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(mg/L)	(mg/L)	%	
0	285	150	47	-	157	127	19	-
200	285	89	69	0.41	157	122	22	0.04
400	285	88	69	0.41	157	115	27	0.09
600	285	102	64	0.32	157	114	27	0.10
800	285	102	64	0.32	157	120	24	0.06
1000	285	107	62	0.29	157	114	27	0.10

3. DEaqs (pH 10)

Dosage	SS			Coagulation Activity		Turbidity		Coagulation Activity	Colour			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(NTU)	(NTU)	%		(mg/L)	(mg/L)	%	
0	125	60	52	-	64.4	36.40	43	-	268	123	54	-
200	125	34	73	0.43	64.4	16.20	75	0.55	268	132	51	-0.07
400	125	48	62	0.20	64.4	19.20	70	0.47	268	133	50	-0.08
600	125	49	61	0.18	64.4	27.40	57	0.26	268	141	47	-0.15
800	125	54	57	0.10	64.4	32.80	49	0.10	268	131	51	-0.07
1000	125	58	54	0.03	64.4	35.40	45	0.03	268	137	49	-0.11

Dosage	COD			Coagulation Activity	NH_3-N			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(mg/L)	(mg/L)	%	
0	285	107	62	-	157	116	26	-
200	285	78	73	0.27	157	97	38	0.16
400	285	84	71	0.21	157	100	36	0.14
600	285	100	65	0.07	157	110	30	0.05
800	285	87	69	0.19	157	115	27	0.01
1000	285	77	73	0.28	157	122	22	-0.05

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4. DEaqs (pH 12)

Dosage	SS			Coagulation Activity	Turbidity			Coagulation Activity	Colour			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(NTU)	(NTU)	%		(mg/L)	(mg/L)	%	
0	125	20	84	-	64.4	14.70	77	-	187	116	38	-
200	125	7	94	0.65	64.4	3.70	94	0.75	187	98	48	0.16
400	125	9	93	0.55	64.4	4.99	92	0.66	187	95	49	0.18
600	125	8	94	0.60	64.4	5.01	92	0.66	187	99	47	0.15
800	125	4	97	0.80	64.4	4.42	93	0.70	187	98	48	0.16
1000	125	6	95	0.70	64.4	6.06	91	0.59	145	93	36	0.20

Dose	COD			Coagulation Activity	NH_3-N			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(mg/L)	(mg/L)	%	
0	197	82	58	-	157	91	42	-
200	197	75	62	0.09	157	89	43	0.02
400	197	78	60	0.05	157	83	47	0.09
600	197	84	57	-0.02	157	88	44	0.03
800	197	89	55	-0.09	157	88	44	0.03
1000	181	132	27	-0.61	170	88	44	0.03

5. DEpowd (pH 10)

Dosage	SS			Coagulation Activity	Turbidity			Coagulation Activity	Colour			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(NTU)	(NTU)	%		(mg/L)	(mg/L)	%	
0	123	65	47	-	63.3	36.00	43	-	799	495	38	-
200	123	37	70	0.43	63.3	14.00	78	0.61	799	503	37	-0.02
400	123	41	67	0.37	63.3	14.00	78	0.61	799	511	36	-0.03
600	123	44	64	0.32	63.3	17.10	73	0.53	799	511	36	-0.03
800	123	46	63	0.31	63.3	30.40	52	0.16	799	519	35	-0.05
1000	123	60	51	0.08	63.3	31.65	50	0.11	799	520	35	-0.05

Dose	COD			Coagulation Activity	NH_3-N			Coagulation Activity
	INITIAL	FINAL	REMOVAL		INITIAL	FINAL	REMOVAL	
(mg/L)	(mg/L)	(mg/L)	%		(mg/L)	(mg/L)	%	
0	294	250	15	-	145	135	7	-
200	294	215	27	0.14	145	115	21	0.15
400	294	230	22	0.08	145	117	19	0.13
600	294	236	20	0.06	145	125	14	0.07
800	294	235	20	0.06	145	128	12	0.05
1000	294	244	17	0.02	145	137	5	-0.01

APPENDIX E: COAGULANT AIDS

(a) DEaqs and DEpowd as a coagulant aid in KSLS

1. DEaqs + 1000 mg/L PACI

Dosage	SS			Turbidity			Colour		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
0	272	122	55	60.50	30.25	50	2712	1492	45
100	272	38	86	60.50	18.75	69	2712	1220	55
500	272	33	88	60.50	14.50	76	2712	651	76
1000	272	49	82	60.50	14.50	76	2712	705	74
1500	272	65	76	60.50	15.10	75	2712	678	75
2000	272	95	65	60.50	17.55	71	2712	678	75

Dosage	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
0	858	558	35	1040	811	22
100	858	480	44	1040	749	28
500	858	386	55	1040	707	32
1000	858	429	50	1040	811	22
1500	858	438	49	1040	832	20
2000	858	429	50	1040	842	19

2. DEaqs + 2000 mg/L PACI

Dosage	SS			Turbidity			Colour		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
0	272	133	51	60.50	33.25	45	2712	1166	57
100	272	71	74	60.50	29.05	52	2712	1031	62
500	272	65	76	60.50	21.10	65	2712	949	65
1000	272	57	79	60.50	16.95	72	2712	705	74
1500	272	76	72	60.50	18.15	70	2712	759	72
2000	272	82	70	60.50	18.15	70	2712	759	72

Dosage	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
0	858	541	37	1040	780	25
100	858	523	39	1040	780	25
500	858	506	41	1040	770	26
1000	858	429	50	1040	738	29
1500	858	446	48	1040	780	25
2000	858	455	47	1040	780	25

3. DEpowd + 1000 mg/L PACI

Dosage	SS			Turbidity			Colour		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
0	272	114	58	60.50	34.45	43	2712	1085	60
100	272	92	66	60.50	27.20	55	2712	1031	62
500	272	73	73	60.50	16.30	73	2712	678	75
1000	272	63	77	60.50	29.65	51	2712	922	66
1500	272	98	64	60.50	38.70	36	2712	1031	62
2000	272	103	62	60.50	40.50	33	2712	1112	59

Dosage	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
0	858	695	19	1040	790	24
100	858	669	22	1040	770	26
500	858	472	45	1040	728	30
1000	858	618	28	1040	749	28
1500	858	626	27	1040	770	26
2000	858	626	27	1040	780	25

4. DEpowd + 2000 mg/L PACI

Dosage	SS			Turbidity			Colour		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
0	272	120	56	60.50	32.00	47	2712	1220	55
100	272	122	55	60.50	30.25	50	2712	1031	62
500	272	101	63	60.50	26.00	57	2712	895	67
1000	272	65	76	60.50	15.70	74	2712	705	74
1500	272	103	62	60.50	28.00	54	2712	922	66
2000	272	103	62	60.50	29.00	52	2712	922	66

Dosage	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
0	858	644	25	1040	801	23
100	858	626	27	1040	780	25
500	858	549	36	1040	770	26
1000	858	489	43	1040	738	29
1500	858	635	26	1040	790	24
2000	858	635	26	1040	800	23

(b) DEaqs and DEpowd as a coagulant aid in KLS

1. DEaqs + 500 mg/L PACI

Dosage	SS			Turbidity			Colour		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
0	120	53	56	36.50	9.10	75	252	126	50
50	120	36	70	36.50	6.20	83	252	111	56
100	120	22	82	36.50	5.40	85	252	106	58
150	120	14	88	36.50	4.75	87	252	60	76
200	120	19	84	36.50	6.55	82	252	66	74

Dosage	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
0	285	171	40	170	126	26
50	285	151	47	170	117	31
100	285	128	55	170	112	34
150	285	91	68	170	112	34
200	285	140	51	170	117	31

2. DEaqs + 200 mg/L PACI

Dosage	SS			Turbidity			Colour		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
0	120	60	50	36.50	12.70	65	252	151	40
50	120	54	55	36.50	9.10	75	252	141	44
100	120	34	72	36.50	8.75	76	252	108	57
150	120	6	74	36.50	8.00	78	252	101	60
200	120	3	70	36.50	8.40	77	252	113	55

Dosage	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
0	285	194	32	170	129	24
50	285	171	40	170	124	27
100	285	154	46	170	121	29
150	285	148	48	170	122	28
200	285	151	47	170	122	28

3. DEpowd + 500 mg/L PACI

Dosage	SS			Turbidity			Colour	
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL
(mg/L)	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)
0	120	54	55	36.50	9.90	73	252	129
50	120	47	61	36.50	8.40	77	252	116
100	120	29	76	36.50	7.70	79	252	106
150	120	25	79	36.50	7.30	80	252	71
200	120	26	78	36.50	9.90	73	252	76

Dosage	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
0	285	185	35	170	136	20
50	285	151	47	170	133	22
100	285	143	50	170	128	25
150	285	97	66	170	122	28
200	285	114	60	170	124	27

4. DEpowd + 200 mg/L PACI

Dosage	SS			Turbidity			Colour		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(NTU)	(NTU)	%	(mg/L)	(mg/L)	%
0	120	67	44	36.50	12.75	65	252	151	40
50	120	60	50	36.50	11.65	68	252	144	43
100	120	38	68	36.50	9.80	73	252	131	48
150	120	34	72	36.50	9.80	73	252	103	59
200	120	38	68	36.50	9.80	73	252	111	56

Dosage	COD			NH_3-N		
	INITIAL	FINAL	REMOVAL	INITIAL	FINAL	REMOVAL
(mg/L)	(mg/L)	(mg/L)	%	(mg/L)	(mg/L)	%
0	285	200	30	170	141	17
50	285	185	35	170	138	19
100	285	157	45	170	132	22
150	285	151	47	170	129	24
200	285	154	46	170	136	20

(c) Floc formation and breakage

1. 2000 mg/L PACI

		Diameter (µm)		
PHASE		$D_{0.1}$	$D_{0.5}$	$D_{0.9}$
1st	$Size_1$	11.71	27.22	55.19
	$Size_2$	11.62	25.92	57.15
	$Size_3$	12.22	24.85	50.87
2nd	$Size_2$	11.32	24.60	50.75
	$Size_3$	11.40	23.55	54.71
3rd	$Size_2$	11.25	23.42	52.82
	$Size_3$	11.49	23.15	53.18

2. 2000 mg/L PACI + 1000 mg/L DEaqs

		Diameter (μm)		
PHASE		$D_{0.1}$	$D_{0.5}$	$D_{0.9}$
1st	$Size_1$	11.78	26.15	54.75
	$Size_2$	11.82	27.43	53.89
	$Size_3$	11.95	27.93	55.31
2nd	$Size_2$	12.10	28.98	55.43
	$Size_3$	12.21	29.41	55.61
3rd	$Size_2$	11.78	29.25	56.37
	$Size_3$	11.80	29.03	54.87

3. 1000 mg/L PACI + 500 mg/L DEaqs

		Diameter (μm)		
PHASE		$D_{0.1}$	$D_{0.5}$	$D_{0.9}$
1st	$Size_1$	11.69	22.81	50.23
	$Size_2$	11.58	28.28	56.48
	$Size_3$	11.88	27.37	59.45
2nd	$Size_2$	11.61	28.10	59.45
	$Size_3$	11.92	28.30	58.39
3rd	$Size_2$	11.90	27.60	55.38
	$Size_3$	11.78	27.35	54.83

(d) Sediment percentage

Volume (mL)	2000 mg/L PACI	2000 mg/L PACI + 1000 mg/L DEaqs	1000 mg/L PACI + 500 mg/L DEaqs
V_0	500	500	500
V_{30}	200	180	150
V_{60}	180	150	125
SP (%)	36	30	25

LIST OF PUBLICATIONS

I) Journals

Zainol, N.A., Aziz, H.A. and Yusoff, M.S. (2011) The use of polyaluminum chloride for the treatment of landfill leachate via coagulation and flocculation processes. Research Journal of Chemical Sciences, 1(3), 34-39.

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II) Conferences

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Zainol, N.A., Aziz, H.A. and Yusoff, M.S. (2012) Leachate characterization at Kuala Sepetang and Kulim landfills: A comparative study. In : The 2nd International Malaysia-Ireland Joint Symposium on Engineering, Science and Business (IMiEJS) 2012 on 18 – 20 June 2012, Putra World Trade Centre (PWTC), Kuala Lumpur, Malaysia.

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